Catalysis Today 158 (2010) 310–316

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Sustainable production of acrolein: Acidic binary metal oxide catalysts for gas-phase dehydration of glycerol

Li-Zhi Tao, Song-Hai Chai[1], Yi Zuo[2], Wen-Tao Zheng, Yu Liang, Bo-Qing Xu*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Available online 4 May 2010

Keywords:
Glycerol dehydration
Acrolein
Binary metal oxides
Solid acids
Green chemistry
Chemicals from polyols

ABSTRACT

Acidic binary metal oxide catalysts, including SnO_2–TiO_2, SnO_2–ZrO_2, TiO_2–Al_2O_3, SiO_2–TiO_2, ZrO_2–SiO_2, ZnO–TiO_2 and TiO_2–ZrO_2, were prepared and employed to catalyze the dehydration reaction of glycerol (GL) at 315 °C. Correlation of the catalyst acidities with their catalytic performance demonstrated that the strongly acidic sites at $-8.2 < H_0 \leq -3.0$ were efficient for the selective production of acrolein (AC) from aqueous GL (10 mol% or 36.2 wt% GL). Micropores in the catalyst textures showed a negative effect on AC selectivity, probably by inducing secondary reactions of AC. The highest AC selectivity obtained over these binary oxide catalysts was in the range between 45 mol% and 52 mol%. A direct use of the anhydrous GL, instead of the aqueous GL, for the dehydration reaction produced much lower AC selectivity but larger amount of heavier products. Among all the catalysts investigated, 10 mol% TiO_2–Al_2O_3 calcined at 600 °C and 50 mol% TiO_2–ZrO_2 calcined at 550 °C exhibited the best catalytic performance for AC production from aqueous GL. The appropriate reaction temperature range for the production of AC was also reported by using this 50 mol% TiO_2–ZrO_2 as a representative catalyst.

1. Introduction

Recently much attention has been paid to the utilization of glycerol (GL), a feedstock molecule derivable from renewable biomass resources, for selective production of value-added chemicals or their intermediates, as depletion of non-renewable fossil resources could happen in a few decades [1–3]. Acrolein (AC), which is an intermediate for the productions of acrylic acid, medicines and other chemical products, can be obtained from a selective double-dehydration of GL, providing a sustainable alternative to the present AC production technology based on petroleum-derived propylene [4–9]. With the understanding that the dehydration reaction of an alcohol would proceed easily in the presence of an acid catalyst and its product selectivity would be dependent of the catalyst acidity, both liquid- and solid-acid catalysts have been screened for AC production from GL dehydration [10–23]. Our earlier investigations using various unsupported and supported solid acid catalysts for the gas-phase dehydration of aqueous GL have identified that the most efficient acidic sites for AC production would be those having the highest acid strength in the range of $-8.2 < H_0 \leq -3.0$ (H_0 being the Hammett acidity function), and Brönsted acid sites are more effective than Lewis acid sites [14]. The representative catalysts met with these requirements included hydrated niobium oxide ($Nb_2O_5 \cdot H_2O$) [15], solid phosphoric acid [9,14], tungstated zirconia (WO_3/ZrO_2) [10,14,23] as well as supported heteropolycids [13,14,16,17,19,21], over which the selectivity of AC can be up to 70 mol% at ca. 315 °C when the concentration of aqueous GL was 10 mol% (36.2 wt%). Higher AC selectivity could be reached by lowering the concentration of GL in the aqueous reaction feed [13,23].

Binary metal oxides are known as an important class of solid acid catalysts with tunable acidity for varied reactions [24]. The literature examples of binary oxide catalysts having acidity at $H_0 \leq -3.0$ include SnO_2–TiO_2, TiO_2–Al_2O_3 and SiO_2–TiO_2 for butene isomerization [25–27], SnO–ZrO_2 for cyclopropane ring-opening and 2-butanol dehydration reactions [28], ZnO–TiO_2 for ethylene hydration [29], and TiO_2–ZrO_2 for a non-oxidative dehydrogenation of ethylbenzene [30]. As the number of acid site in a binary oxide is dependent of its composition [24], maximization of the acidity at $H_0 \leq -3.0$ would become possible in a specific composition range. Our literature survey has identified that 50 mol% SnO_2–TiO_2 [25], 10 mol% TiO_2–Al_2O_3 [26], 50 mol% SiO_2–TiO_2 [27], 10 mol% SnO–ZrO_2 [28], and 50 mol% TiO_2–ZrO_2 [30,31] were among those materials with such maximized acidity. In order to gain an insight into the potential of binary oxide catalysts for AC production from GL, these binary oxides are prepared and used as the catalysts in this present work to catalyze the GL dehydration reaction. The reaction is conducted mostly using aqueous GL

---

* Corresponding author. Tel.: +86 10 62792122; fax: +86 10 62792122.
E-mail address: bqxu@mail.tsinghua.edu.cn (B.-Q. Xu).

[1] Present address: Berkeley Catalysis Center, Department of Chemical Engineering, University of California at Berkeley, CA 94720, USA.

[2] A graduate student on leave from School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China.

0920-5861/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.073

Table 1
Texture and acidity data of the investigated binary metal oxide catalysts.

Catalyst	Texture properties			Acidity ($mmol\,g^{-1}$)			Fractional strong acidity[a]
	SA[b] ($m^2\,g^{-1}$)	PV[c] ($cm^3\,g^{-1}$)	PD[d] (nm)	$-8.2 < H_0 \leq -3.0$	$-3.0 < H_0 \leq +6.8$	Total acitidy	
50SnTi-500	107	0.16	6.0	0	0.27	0.27	0
50SnTi-650	67	0.16	9.3	0	0.23	0.23	0
10SnZr-500	65	0.08	4.7	0	0.03	0.03	0
10SnZr-650	41	0.12	11.2	0	0.02	0.02	0
10TiAl-500	352	0.40	4.6	0.08	0.27	0.35	0.23
10TiAl-600	303	0.41	5.4	0.28	0.19	0.47	0.60
50SiTi-500	304	0.21	2.7	0.73	0.63	1.36	0.54
50SiTi-700	124	0.09	3.0	0.60	0.50	1.10	0.55
20ZrSi-500	421	0.29	2.7	0.57	1.30	1.87	0.30
75ZrSi-500	205	0.12	2.3	0.18	0.33	0.51	0.35
31ZnTi-350	264	0.23	3.4	0.50	1.10	1.60	0.31
50TiZr-550	257	0.53	3.5	0.49	1.05	1.54	0.32
50TiZr-450	314	0.56	3.2	–	–	–	–
50TiZr-650	118	0.39	6.0	–	–	–	–
50TiZr-800	30	0.18	19	–	–	–	–

[a] Fractional acidity at $-8.2 < H_0 \leq -3.0$.
[b] BET surface area.
[c] Pore volume measured at $P/P_0 = 0.995$.
[d] Average pore diameter measured from the desorption branch according to the BJH method.

(10 mol% GL) as the reaction feed at 315 °C with a high GL space velocity ($400\,h^{-1}$). The effect of reaction temperature and influence of catalyst calcination temperature on AC formation from GL are also reported using a TiO_2–ZrO_2 sample containing equal molar numbers of TiO_2 and ZrO_2. For the comparison purpose, anhydrous "pure" GL was also reacted over a few selected catalysts.

2. Experimental

2.1. Catalyst preparation

A total of 12 binary metal oxide catalysts were investigated in this work, including SnO_2–TiO_2, SnO_2–ZrO_2, TiO_2–Al_2O_3, SiO_2–TiO_2, ZrO_2–SiO_2, ZnO–TiO_2 and TiO_2–ZrO_2. These samples were prepared by co-precipitation from their metal salts using aqueous ammonia (2 wt% $NH_3{\cdot}H_2O$ in water) as the precipitation agent at room temperature, except for those TiO_2-conatining samples which were precipitated at the freezing temperature (0 °C), using an ice-water bath. The precursor salts for SnO_2, TiO_2, ZrO_2, SiO_2, Al_2O_3 and ZnO were $SnCl_4{\cdot}9H_2O$, $TiCl_4$, $ZrOCl_2{\cdot}8H_2O$, $Si(OC_2H_5)_4$, $Al(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$, respectively. The obtained precipitates were washed repeatedly with double deionized water until chloride ions in the filtrate were not detectable with excessive 0.01 M $AgNO_3$ solution. A further washing with anhydrous ethanol for 4 times was also conducted for the TiO_2–ZrO_2 precipitates. The washed samples were then dried overnight at 110 °C, followed by calcination at elevated temperatures (T °C) for 5 h in flowing nitrogen for TiO_2–ZrO_2 and in flowing air for the other samples. According to the calcination temperature T and the molar percentage of the former component (x mol%), the obtained catalysts were denoted as xM1M2-T. For example, 50SnTi-500 and 10SnZr-650 refer to the SnO_2–TiO_2 sample containing 50 mol% SnO_2 and SnO_2–ZrO_2 containing 10 mol% SnO_2; the calcination temperature was 500 °C for the SnO_2–TiO_2 but 650 °C for the SnO_2–ZrO_2 sample.

2.2. Characterizations

Measurements of catalyst acidity (acid strength and amount) were based on the n-butylamine titration method using Hammett indicators, including anthraquinone (pKa = −8.2), dicinnamalacetone (pKa = −3.0), and neutral red (pKa = 6.8). Details of these measurements were described earlier in previous literature [14]. The acid strength was expressed by Hammett acidity function (H_0) scaled by pKa values of the indicators. Before the measurement, the samples were formulated into fine powders (100–180 mesh) and pretreated at 315 °C for 4 h in flowing dry N_2.

BET surface area, pore volume, and average pore diameter of the binary oxide samples were derived from the nitrogen adsorption–desorption isotherms measured at 77 K on a Micromeritics ASAP 2010C instrument. The samples were dehydrated under vacuum at 200 °C for 5 h prior to the measurement. The average pore diameter data were calculated according to the well-known Barrett–Joyner–Halenda (BJH) method, using the desorption branch.

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with a Ni-filtered CuKα ($\lambda = 0.15406$ nm) radiation source working at 40 kV and 40 mA.

2.3. Catalytic reaction

The gas-phase dehydration reaction of GL was carried out at 315 °C under atmospheric pressure in a vertical fixed-bed tubular quartz reactor (i.d. 9 mm, length 50 cm), which was heated by a tubular furnace in a height of 40 cm [14–16]. A constant volume (0.63 ml) of the catalyst bed was sandwiched in the middle of the reactor by quartz wool packs. Two millilitre quartz sands (2 cm in height) were placed above the catalyst bed for complete evaporation of the reactants. Prior to the reaction, the catalyst was pretreated at the reaction temperature for 1.5 h in flowing dry nitrogen ($30\,ml\,min^{-1}$). The reaction feed, an aqueous solution of GL (10 mol% or 36.2 wt% GL in water) or "anhydrous" GL reagent, was fed continuously into the reactor inlet (top of the reactor tube) by a micro-pump at a gas hourly space velocity (GHSV) of $400\,h^{-1}$ by GL. Dry nitrogen ($17.8\,ml\,min^{-1}$) was used as a carrier gas when "anhydrous" GL was directly used as the reaction feed while no carrier gas was added when aqueous GL was the reaction feed.

The reaction products were condensed in an ice-water 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 [14–16,21]. The reaction was continued for 10 h. The GL conversion and product

Table 2
Catalytic performance of binary metal oxides for gas-phase dehydration of aqueous glycerol (10 mol%) at 315 °C.

Catalyst (0.63 ml)	TOS = 1–2 h		TOS = 9–10 h	
	GL conversion (%)	AC selectivity (mol%)	GL conversion (%)	AC selectivity (mol%)
50SnTi-500	81	19	78	16
50SnTi-650	70	16	37	20
10SnZr-500	34	5	20	7
10SnZr-650	18	6	17	6
10TiAl-500	72	32	42	40
10TiAl-600	86	43	67	52
50SiTi-500	44	42	12	24
50SiTi-700	30	40	12	40
20ZrSi-500	75	35	35	15
75ZrSi-500	62	30	25	21
31ZnTi-350	90	34	42	45
50TiZr-550	78	40	60	45

selectivity data were calculated according to the following equations:

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

$$\text{Product selectivity}\,(\text{mol\%}) = \frac{\text{Moles of carbon in a product defined}}{\text{Moles of carbon in glycerol reacted}} \times 100$$

3. Results and discussion

3.1. Textural and acidic properties

Table 1 shows the texture and acidity data of the binary metal oxides prepared in this study. The textural data for the 50SnTi, 10SnZr, 31ZnTi, 10TiAl, 50SiTi and 50TiZr samples were close to those reported in Refs. [25,28,29,26,27,30], respectively. However, our present 20ZrSi-500 and 75ZrSi-500 samples showed much higher specific surface areas than those in Ref. [32]. For the samples having the same compositions, the one calcined at a higher temperature would show a smaller specific surface area and pore volume but larger pore diameter than its counterpart sample calcined at a lower temperature. Judging from the average pore diameter data, mesopores would dominate in the textures of our binary metal oxides except for the SiTi and ZrSi samples, whose small average pore diameters (2.0–3.0 nm) could imply that micropores (diameter ≤ 2.0 nm) were significant to their textures.

The 50SnTi-500 and -650 as well as 10SnZr-500 and -650 samples showed no strong acidity at $H_0 \leq -3.0$ but only weak and medium strong ones at $-3.0 < H_0 \leq +6.8$. These acidity data are at variances of earlier documentations [25,28] although the compositions and calcination temperatures of these binary metal oxides were chosen in attempts to maximize the strong acidity according to the references. Since this present work aims to investigate their catalytic performance for GL dehydration, we made no attempt to uncover other factors that could be responsible for such differences.

All of the other samples showed acidities at $-3.0 < H_0 \leq +6.8$ as well as $-8.2 < H_0 \leq -3.0$, in qualitatively consistent with the earlier literature [26,27,29–31]. For the two TiO_2–Al_2O_3 samples, the total acidity on 10TiAl-600 was 0.47 mmol g^{-1}, which is 0.12 mmol g^{-1} higher than the acidity on its counterpart 10TiAl-500. The number of strongly acidic sites ($-8.2 < H_0 \leq -3.0$) on 10TiAl-600 was 0.28 mmol g^{-1}, which is 0.20 mmol g^{-1} higher than the number on 10TiAl-500. The numbers of strongly acidic sites on the TiO_2–SiO_2 samples were higher than those reported by Itob et al. [27]; the present 50SiTi-500 showed a number of 0.73 mmol g^{-1} while the reported number in Ref. [27] was 0.50 mmol g^{-1} for the strong acidity at $-8.2 < H_0 \leq -3.0$. The acidity data on the present two ZrO_2–SiO_2 samples (20ZrSi-500 and 75ZrSi-500) seem to be good examples in showing the important effect of composition on the acidity of a binary metal oxide; the strong acidity at $-8.2 < H_0 \leq -3.0$ was as high as 0.57 mmol g^{-1} on 20ZrSi-500 while the number was reduced to one-third (0.18 mmol g^{-1}) on 75ZrSi-500. The present ZnO–TiO_2 (31ZnTi-350) and TiO_2–ZrO_2 (50TiZr-550) samples showed also relatively high numbers of the strongly acidic sites (ca. 0.5 mmol g^{-1} at $-8.2 < H_0 \leq -3.0$), agreeing well with those documented in Refs. [29,31].

Presented in the last column of Table 1 are the data of fractional strong acidity on each sample, which is defined as the percentage of strong acidity at $-8.2 < H_0 \leq -3.0$ to the total acidity at $H_0 \leq +6.8$,

Table 3
Product distribution over the investigated binary metal oxide catalysts at 315 °C and TOS = 9–10 h[a].

Catalyst (0.63 ml)	GL conversion (%)	Product selectivity at TOS = 9–10 h (mol%)				
		Acrolein	Acetaldehyde	Allyl alcohol	1-Hydroxy-acetone	Unknowns
50SnTi-500	78	16	3	8	15	58
50SnTi-650	37	20	3	6	16	55
10SnZr-500	20	7	1	2	23	67
10SnZr-650	17	6	1	1	24	68
10TiAl-500	42	40	3	2	15	40
10TiAl-600	67	52	3	2	17	26
50TiSi-500	12	24	2	1	9	64
50TiSi-700	12	40	2	1	13	44
20ZrSi-500	35	15	5	1	8	71
75ZrSi-500	25	21	4	1	14	60
31ZnTi-350	42	45	3	1	20	31
50TiZr-550	60	45	5	3	17	30

[a] Reaction feed: 10 mol% glycerol in water.

since this fractional number seems to be important for the formation of AC from GL [14,15].

3.2. Binary metal oxide catalysts for gas-phase dehydration of glycerol

3.2.1. Catalytic dehydration reaction using aqueous glycerol

Table 2 shows the catalytic performance of the binary metal oxide catalysts for the gas-phase dehydration of aqueous GL at 315 °C and GHSV by GL of 400 h^{-1} under ambient pressure. The differences in GL conversion and AC selectivity data at TOS (time-on-stream) = 1–2 h and 9–10 h would characterize the catalytic stability of the binary metal oxide catalysts during the reaction [14,15]. In reference to the acidity data given in Table 1, it is clear that the catalysts with non-measurable strong acidity at $-8.2 < H_0 \leq -3.0$ showed usually very low AC selectivity. The selectivity of AC over the two 50SnTi catalysts was no higher than 20 mol% while that over both 10SnZr catalysts with almost no acidity was even lower than 7 mol%. In addition to the lack of strongly acidic sites, a possible presence of basic sites at the surface of SnO_2–ZrO_2 samples [28] may have also relation with the very low AC selectivity over the 10SnZr catalysts since basic sites were found not effective for the formation of AC [14].

On the other hand, the binary metal oxide catalysts having considerable numbers of strongly acidic sites ($-8.2 < H_0 \leq -3.0$) produced reasonably high AC selectivity (>40 mol%) except for the 50SiTi, 20ZrSi and 75ZrSi samples. As it was mentioned in the previous section, these later catalysts had significant micropores (diameter ≤ 2.0 nm) in their textures, which could lower the diffusivity of the as-formed AC molecules and promote their secondary reactions because of steric hindrance [14], leading to low AC selectivity. In consistence with this explanation, these catalysts showed also much higher deactivation rates as one would judge from the huge differences between the GL conversion levels at TOS = 1–2 h and 9–10 h (Table 2).

Table 3 gives the product distribution data at TOS = 9–10 h over all of the binary metal oxide catalysts. In agreement with our earlier data on supported and unsupported typical solid acid catalysts [14–16,21], 1-hydroxylacetone, allyl alcohol and acetaldehyde appeared also as the main by-product in the dehydration of aqueous GL over these binary metal oxide catalysts. The distinctly higher selectivity for 1-hydroxylacetone (23–24 mol%) over both 10SnZr samples would suggest that some basic sites were indeed involved in the dehydration reaction over these SnO_2–ZrO_2 catalysts since cooperative acid–base bifunctional properties would be more effective in inducing the required mono-dehydration reaction from either hydroxyls at the terminal carbon atoms of a GL molecule. The basic sites could serve to abstract a proton from the central carbon. In support of this assumption, the gas-phase dehydration of GL over the typical acid–base bifunctional ZrO_2 catalysts [33,34] produced even much higher selectivity for 1-hydroxylacetone (28%) [14,16]. Moreover, the selectivity data of 1-hydroxyacetone over the other binary metal oxide catalysts (15–20 mol%) seem also higher compared with those obtained over the well investigated solid phosphoric acid [9,14], tungstated zirconia (WO_3/ZrO_2) [10,14,23], and supported heteropolycids [13,14,16,17,19,21] catalysts. This higher selectivity for the formation of 1-hydroxyacetone would further hint that basic sites on these binary metal oxide catalysts were also involved in the GL dehydration reactions. This explanation would also account for the present observation that the binary metal oxide catalysts failed to produce a higher AC selectivity than those supported typical Brönsted acid catalysts in the recent literature [13,14,16,17,19,21] as the co-presence of basic sites, though not measured in the present study, would be inevitable at the surface of binary metal oxide catalysts [26–28].

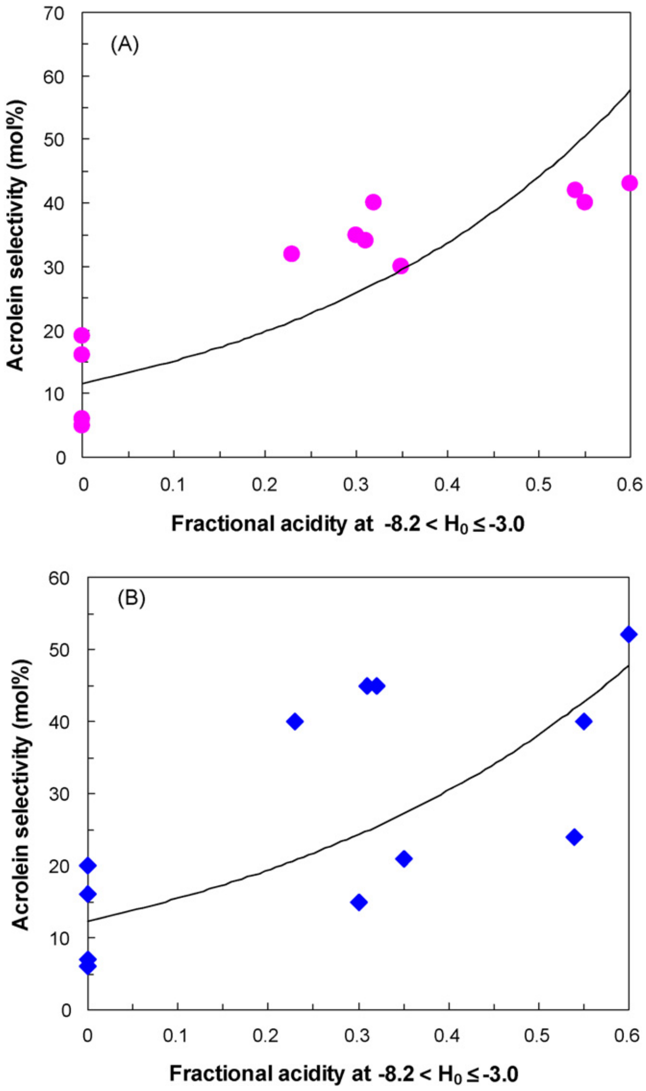

Fig. 1. Correlation between the catalyst fractional acidity at $-8.2 < H_0 \leq -3.0$ and acrolein selectivity at (A) TOS = 1–2 h and (B) TOS = 9–10 h.

Solid acids with weak and medium strong acidity (i.e., $-3.0 < H_0 \leq +6.8$) were defined as Group-2 while those with strong acidity (i.e., $-8.2 < H_0 \leq -3.0$) as Group-3 catalysts for the gas-phase GL dehydration reaction in our earlier work [14]. We attempt to correlate in Fig. 1 the AC selectivity at TOS = 1–2 h and 9–10 h with the fractional acidity at $-8.2 < H_0 \leq -3.0$ for all of the binary oxide catalysts investigated in this study. Although such correlations could be disturbed by the co-presence of basic sites at the catalyst surfaces, the trend is clear in showing that the strong acidity would favor the selective formation of AC from the aqueous GL. Thus, the catalytic data of this present work are basically in support of our earlier observations that the formation of AC is favorable over the catalysts whose strongest acidities are at $-8.2 < H_0 \leq -3.0$ [14,15].

3.2.2. Gas-phase dehydration of anhydrous glycerol

Anhydrous “pure” GL was also employed, instead of aqueous GL, as the reaction feed to understand the effect of water dilution. Table 4 gives the product distribution at TOS = 9–10 h over a few selected catalysts. As long as the nature of unidentified products was not concerned, the product selectivity data over the 50SnTi and 10SnZr catalysts with no strong acidity at $-8.2 < H_0 \leq -3.0$ appeared similar to those when the aqueous feed (10 mol% GL) was used for the reaction (Table 3). However, the selectivity data

Table 4
Product distribution over the investigated binary metal oxides at 315 °C and TOS = 9–10 h[a].

Catalyst (0.63 ml)	GL conversion (%)	Product selectivity at TOS = 9–10 h (mol%)				
		Acrolein	Acetaldehyde	Allyl alcohol	1-Hydroxy-acetone	Unknowns
50SnTi-650	59	22	2	5	16	55
10SnZr-500	51	8	1	2	12	77
10TiAl-500	45	26	3	1	8	62
10TiAl-600	57	26	3	2	8	61

[a] Reaction feed: anhydrous "pure" glycerol; glycerol/N_2 partial pressure: 20 kPa/80 kPa.

for AC as well 1-hydroxylacetone were remarkably lowered over the binary metal oxides catalysts having the strong acidity at $-8.2 < H_0 \leq -3.0$, as exemplified in Table 4 for both 10TiAl catalysts. In contrast, the use of anhydrous GL for the reaction resulted in the formation of significantly larger amount of heavier products, whose identities remained unidentified at this stage. These results suggest that a co-feeding of water (or dilution with steam) during the reaction has a positive effect on AC production. This positive effect of water molecules might be arisen from water inhibition on coking, which was well-known in a number of other acid-catalyzed dehydration reactions [35–37].

3.3. Dehydration of aqueous glycerol over TiO_2–ZrO_2 catalysts

TiO_2–ZrO_2 is a binary oxide catalyst with interesting acid–base catalysis properties [24]. This binary oxide catalyst is known to show the highest acidity at the molar ratio of Ti/Zr = 1/1 (50TiZr), and depending on the final calcination temperature for its preparation the acidity at $-8.2 < H_0 \leq -3.0$ could be as high as ca. 0.3–0.6 mmol/g [31]. The 50TiZr sample was used to investigate the effects of catalyst calcination temperature and reaction temperature on the dehydration of aqueous GL for AC production.

Fig. 2 shows the powder XRD patterns of 50TiZr-*T* samples. The textural properties derived from the nitrogen adsorption–desorption isotherms were tabulated in Table 1. The samples with *T* = 450 °C and 550 °C appeared as amorphous materials since no distinct X-ray diffraction was detected. Clear diffractions at $2\theta = 24.8°$ and 30.6° for $ZrTiO_4$ crystallites [31] were detected when the calcination temperature was increased to *T* = 650 °C (50TiZr-650). The diffractions for $ZrTiO_4$ became narrowed and sharper on further increasing the calcination temperature up to *T* = 800 °C (50TiZr-800), indicating a continued $ZrTiO_4$ crystallite growth. The weak diffractions at $2\theta = 32.6°$, 35.8° and 42.0° on the XRD patterns for both 50TiZr-650 and -800 samples were associated also with the $ZrTiO_4$ crystallites [31].

Fig. 3 shows the time courses for GL conversion (Fig. 3A) and AC selectivity (Fig. 3B) during the dehydration of aqueous GL over the 50TiZr-*T* catalysts of *T* = 450–800 °C. Except the reaction over the 50TiZr-800 catalyst, the reaction time courses featured a continued decrease in GL conversion with the reaction TOS and an induction period of 3–4 h for AC selective formation, which are similar to our earlier observations with other typical solid acid catalysts [14–16,21]. The increase in *T* up to 800 °C led to a decrease in GL conversion especially at *T* > 650 °C; the conversion of GL was the highest over the catalyst of *T* = 450 °C (50TiZr-450) but lowest over the one of *T* = 800 °C (50TiZr-800). However, this least active 50TiZr-800 catalyst exhibited also the slowest deactivation rate.

It is clearly seen that the catalyst of *T* = 550 °C (50TiZr-550) produced the highest AC selectivity (45 mol%) while this selectivity

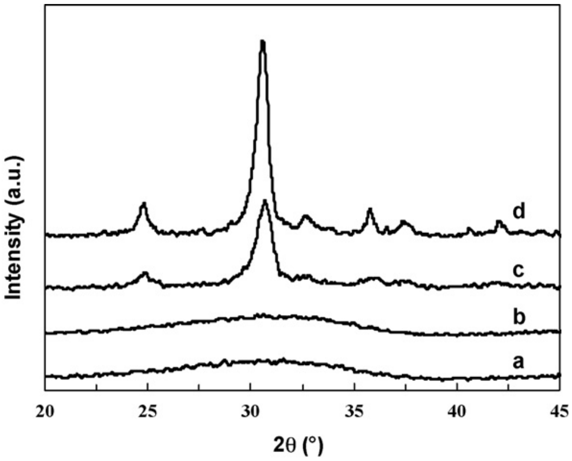

Fig. 2. XRD patterns of 50TiZr samples calcinated at (a) 450 °C, (b) 550 °C, (c) 650 °C, and (d) 800 °C.

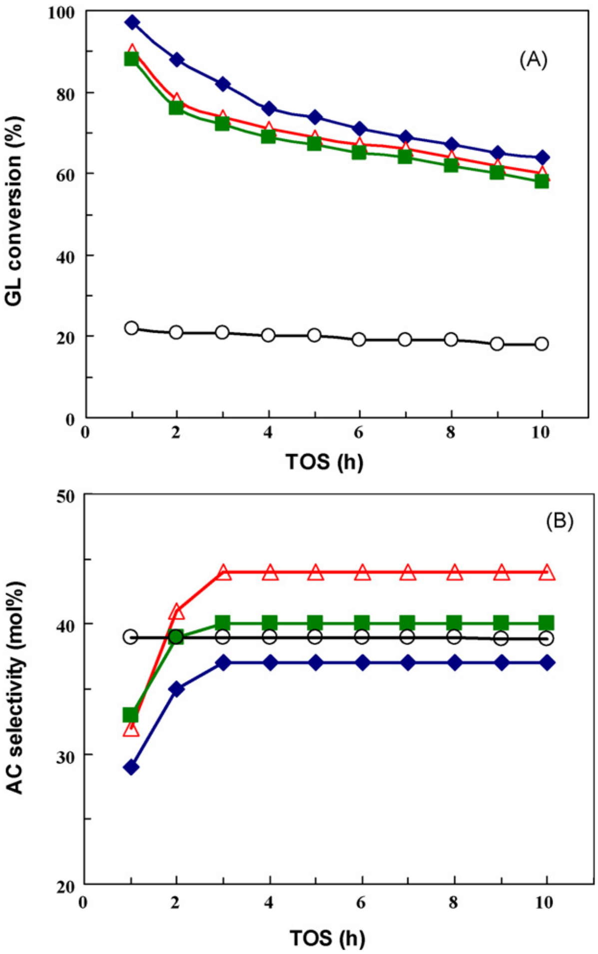

Fig. 3. Time courses of (A) glycerol conversion and (B) acrolein selectivity over the 50TiZr catalysts calcinated at (♦) 450 °C, (△) 550 °C, (■) 650 °C, and (○) 800 °C.

Table 5
Product distribution over TiO_2–ZrO_2 binary metal oxides at 315 °C and TOS = 9–10 h[a].

Catalyst (0.63 ml)	GL conversion (%)	Product selectivity at TOS = 9–10 h (mol%)				
		Acrolein	Acetaldehyde	Allyl alcohol	1-Hydroxylacetone	Unknowns
50TiZr-450	64	38	5	3	17	37
50TiZr-550	60	45	5	3	17	30
50TiZr-650	58	41	4	3	19	33
50TiZr-800	18	39	2	2	26	31

[a] The reaction feed was 10 mol% glycerol in water.

Table 6
Effect of reaction temperature on product distribution over 50TiZr-550 catalyst[a].

Reaction temperature (°C)	GL conversion (%)	Product selectivity at TOS = 9–10 h (mol%)				
		Acrolein	Acetaldehyde	Allyl alcohol	1-Hydroxylacetone	Unknowns
315	60	45	5	3	17	30
350	67	48	7	2	13	30
400	17	39	11	2	9	39

[a] The reaction feed was 10 mol% glycerol in water.

was the lowest over the 50TiZr-450 catalyst (38 mol%). The disadvantage of the 50TiZr-650 and -800 catalysts for selective AC production from the aqueous GL would be due to the loss of surface acidity by formation of $ZrTiO_4$ crystallites at temperatures higher than 600 °C. According to Wang et al. [31], the surface acidity by butylamine adsorption of a 1:1 TiO_2–ZrO_2 catalyst would reduce by 50% and then 80% when the catalyst calcination temperature was increased from 550 °C to 650 °C and then to 800 °C.

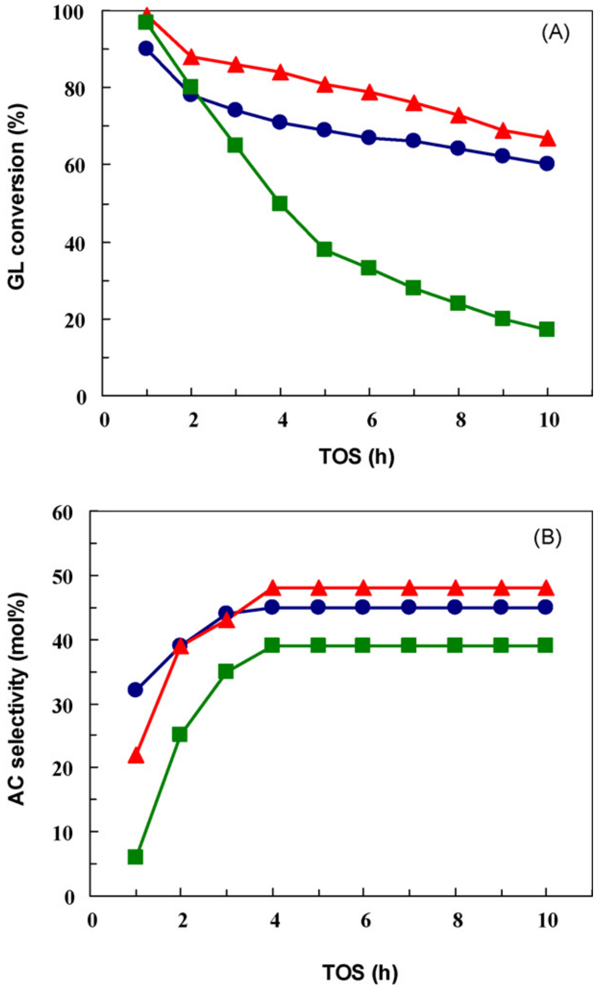

Fig. 4. Time courses of (A) glycerol conversion and (B) acrolein selectivity over 50TiZr-550 catalyst at different reaction temperatures: (●) 315 °C, (▲) 350 °C, and (■) 400 °C.

Table 5 shows the product distribution data at TOS = 9–10 h over the 50TiZr-*T* catalysts. The main by-product 1-hydroxyacetone increased from 17 mol% to 26 mol%, mainly at the expense of the unknowns, when the calcination temperature *T* was increased from 450 °C to 800 °C. The formation of other products seemed insensitive to the change of *T* among these 50TiZr-*T* catalysts.

The data shown in Fig. 4 and Table 6 report on the influence of reaction temperature (315–400 °C) on the performance of 50TiZr-550 catalyst for the dehydration reaction of the aqueous GL. Increasing the reaction temperature to 350 °C from 315 °C benefited the production of AC but a further increase to 400 °C resulted in dramatic catalyst deactivation and significantly lower AC selectivity. Measurement of the carbon deposits by temperature programmed oxidation (TPO) of the reacted catalyst disclosed a number for carbon deposits of 316 mg g-cat^{-1} on the sample reacted at 400 °C, which was almost 1.5 times that on the catalyst reacted at 315 °C (224 mg g-cat^{-1}). Obviously, the dramatic catalyst deactivation during the reaction at 400 °C was a consequence of rapid carbon deposition at the catalyst surface [14,16]. These results suggest that the appropriate reaction temperature for the gas-phase dehydration of aqueous GL to produce AC would be 315–350 °C using the binary metal oxide based solid acid catalysts.

4. Conclusions

The present investigation on the potential of binary metal oxide based solid acid catalysts for the dehydration of aqueous GL further confirms our earlier conclusion that the strongly acidic sites at $-8.2 < H_0 \leq -3.0$ are efficient for the production of AC. In addition to the acidity requirement, micropores in the binary oxide catalysts were shown to produce a negative effect on the selectivity for AC formation, probably by reducing the diffusivity of AC for secondary reactions. Tuning the acidity and pore size distribution of the binary oxide materials could be viable for the development of more efficient catalysts for improving the selectivity of AC production. However, the highest obtainable AC selectivity over the binary oxide catalyst could not be higher than those (ca. 70 mol%) over the typical Brönsted acid catalysts such as supported solid phosphoric acid and heteropolycids [17,24] since a co-presence of basic sites would be inevitable at the surface of the binary oxide based solid acid catalysts.

The use of anhydrous GL for the dehydration reaction produced much lower AC selectivity but larger amount of heavier products in comparison with the dehydration of aqueous GL. The appropriate reaction temperature range for AC production by the dehydration of aqueous GL would be 315–350 °C.

Among the catalysts investigated, the 10TiAl-600 and 50TiZr-550 catalysts showed the best catalytic performance for AC production form aqueous GL; the AC selectivity was as high as 45–52 mol% while the GL conversion was kept higher than 60% during the reaction up to TOS = 10 h at 315 °C with glycerol GHSV of 400 h^{-1}.

Acknowledgement

This work is partly supported by NSF of China (grant: 20590362).

References

[1] D.L. Klass, Biomass for Renewable Energy, Fuels and Chemicals, Academic Press, San Diego, 1998.

[2] H. Van Bekkum, P. Gallezot, Top. Catal. 27 (2004) 1.

[3] G.W. Huber, J.A. Dumesic, Catal. Today 111 (2006) 119.

[4] E. Schwenk, M. Gehrke, F. Aichner, U.S. Patent 1,916,743 (1933), to ScheeringKahlbaum A.-G.

[5] H. Adkins, W.H. Hartung, Org. Synth. Coll. 1 (1941) 15.

[6] S. Ramayya, A. Brittain, C. DeAlmeida, W. Mok, M.J. Antal, Fuel 66 (1987) 1364.

[7] M.J. Antal Jr., W.S.L. Mok, G.N. Richards, Carbohydr. Res. 199 (1990) 111.

[8] T. Hass, A. Neher, D. Arntz, U.S. Patent 5,426,249 (1995), to Degussa Aktiengesellschaft.

[9] A. Neher, T. Haas, D. Arntz, H. Klenk, W. Girke, U.S. Patent 5,387,720 (1995), to Degussa ktiengesellschaft.

[10] (a) J.-L. Dubois, C. Duquenne, W. Hoelderich, F Patent 2,882,052 (2005), to Arkema SA;
(b) J.-L. Dubois, C. Duquenne, W. Hoelderich, J. Kervennal, F Patent 2,882,053 (2005), to Arkema SA;
(c) J.-L. Dubois, C. Duquenne, W. Hoelderich, F Patent 2,884,817 (2005), to Arkema SA;
(d) J.-L. Dubois, C. Duquenne, W. Hoelderich, F Patent 2,884,818 (2006), to Arkema SA.

[11] L. Ott, M. Bicker, H. Vogel, Green Chem. 8 (2006) 214.

[12] M. Watanabe, T. Iida, Y. Aizawa, T.M. Aida, H. Inomata, Bioresour. Technol. 98 (2007) 1285.

[13] E. Tsukuda, S. Sato, R. Takahashi, T. Sodesawa, Catal. Commun. 8 (2007) 1349.

[14] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, Green Chem. 9 (2007) 1130.

[15] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, J. Catal. 250 (2007) 342.

[16] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, Green Chem. 10 (2008) 1087.

[17] H. Atia, U. Armbruster, A. Martin, J. Catal. 258 (2008) 71.

[18] A. Corma, G.W. Huber, L. Sauvanaud, P. O'Connor, J. Catal. 257 (2008) 163.

[19] L. Ning, Y. Ding, W. Chen, L. Gong, R. Lin, Y. Lu, Q. Xin, Chin. J. Catal. 29 (2008) 212.

[20] W. Yan, G.J. Suppes, Ind. Eng. Chem. Res 48 (2009) 3279.

[21] S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, Appl. Catal. A 353 (2009) 213.

[22] Q.-B. Liu, Z. Zhang, Y. Du, J. Li, X.-G. Yang, Catal. Lett. 127 (2009) 419.

[23] A. Ulgen, W. Hoelderich, Catal. Lett. 131 (2009) 122.

[24] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New Solid Acids and Bases: Their catalytic Properties, Kodansha, Tokyo and Elsevier, Amsterdam, 1989.

[25] M. Itob, H. Hattori, K. Tanabe, J. Catal. 43 (1976) 192.

[26] E. Rodenas, H. Hattori, T. Yamaguchi, K. Tanabe, J. Catal. 69 (1981) 434.

[27] M. Itob, H. Hattori, K. Tanabe, J. Catal. 35 (1974) 225.

[28] G.-W. Wang, H. Hattori, K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2407.

[29] K. Tanabe, C. Ishiya, I. Matsuzaki, I. Ichikawa, H. Hattori, Bull. Chem. Soc. Jpn. 45 (1972) 47.

[30] J.-C. Wu, C.-S. Chung, C.-L. Ay, I. Wang, J. Catal. 87 (1984) 98.

[31] I. Wang, W.-F. Chang, R.-J. Shiau, J.-C. Wu, C.-S. Chung, J. Catal. 83 (1983) 428.

[32] J.-A. Anderson, C. Fergusson, R.-R. Inmaculada, G.-R. Antonio, J. Catal. 192 (2000) 344.

[33] B.-Q. Xu, T. Yamaguchi, K. Tanabe, Chem. Lett. 17 (1988) 1663.

[34] B.-Q. Xu, T. Yamaguchi, K. Tanabe, Appl. Catal. 75 (1991) 75.

[35] A.G. Gayubo, A.T. Aguayo, A.L. Moran, M. Olazar, J. Bilbao, AIChE J. 48 (2002) 1561.

[36] A.G. Gayubo, A.T. Aguayo, A. Atutxa, M. Olazar, J. Bilbao, Ind. Eng. Chem. Res. 43 (2004) 2610.

[37] C.B. Phillips, R. Datta, Ind. Eng. Chem. Res. 36 (1997) 4466.