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Highly efficient and robust Mg_{0.388}Al_{2.408}O₄ catalyst for gas-phase decarbonylation of lactic acid to acetaldehyde



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ABSTRACT

The process for decarbonylation of lactic acid into acetaldehyde over magnesium aluminum oxides was explored. Magnesium aluminum oxides were prepared with co-precipitation method by varying pH values, Mg/Al molar ratios and calcination temperatures. The as-prepared magnesium aluminum oxides were characterized by nitrogen adsorption-desorption, XRD, FT-IR, NH₃-TPD, CO₂-TPD and SEM, and were employed to catalyze the gas-phase decarbonylation of lactic acid to produce acetaldehyde. It is found that pH value is a crucial factor for the formation of magnesium aluminum oxides. At pH = 7-8, the obtained magnesium aluminum oxide is indexed to $Mg_{0.388}Al_{2.408}O_4$, while at pH > 8, it is ascribed to MgAl₂O₄ spinel. At low calcination temperature such as 550 °C, Mg_{0.388}Al_{2.408}O₄ can be formed, and it enhances crystallinity with an increase of calcination temperature. However, as the calcination temperature exceeded 1200 °C, the structure of Mg_{0.388}Al_{2.408}O₄ encountered a serious destruction. Comparative study on catalytic performance for Mg_{0.388}Al_{2.408}O₄ and MgAl₂O₄ spinel suggests that the former has more excellent performance than the latter. Besides mixtures including Mg_{0.388}Al_{2.408}O₄ and Al₂O₃, pure MgO and pure Al₂O₃ were also investigated on their catalytic performance. In the presence of $Mg_{0.388}Al_{2.408}O_4$, the stability experiment was performed at high LA LHSV such as 13.0 h⁻¹. Encouragingly, the decarbonylation reaction of lactic acid proceeded efficiently at around 500 h on stream, and acetaldehyde selectivity remained constant (ca. ~93%).

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1. Introduction

In organic synthesis, acetaldehyde is a very important compound and has been utilized as a useful synthon for various important chemicals such as peracetic acid, pentaerythritol, pyridine bases, butyleneglycol, and chloral [1,2]. So far, acetaldehyde is mainly produced via ethylene partial oxidation using PdCl₂-CuCl₂ catalyst. Due to the increasing depletion of petroleum reserves that are used to produce ethylene via high temperature pyrolysis or catalytic cracking, this route on ethylene partial oxidation will be restricted in the near future. For this reason, it has become a heated research that acetaldehyde is produced from the biomass. Several references have recently reported that acetaldehyde is produced via catalytic dehydrogenation of ethanol or partial oxidation of ethanol [1,3-7]. Besides, acetaldehyde is also obtained through decarbonylation of lactic acid (LA) accompanying with co-product of carbon monoxide [8]. However, carbon monoxide is viewed as an important carbonyl synthesis source for the

preparation of carbonyl compounds such as acetic acid, acrylic acid, and other α , β -unsaturated acids via carbonylation reaction of corresponding substrates [9–13]. Carbon monoxide is also used to synthesize propionaldehyde and other aldehydes through hydroformylation reaction of ethylene and other alkenes [14–17]. As a platform molecule, LA is utilized to produce many value added chemicals such as acrylic acid [18-23], acetaldehyde [8], 2,3-pentanedione [24,25], propionic acid [26], pyruvic acid [27] and polylactic acid [28]. Except for corn starch, rich and inexpensive biomass materials such as cellulose [29], sugars [30], and sorbitol [31] have also been used to produce LA. Thus acetaldehyde produced from LA has displayed a potential perspective. However few researches on decarbonylation of LA to acetaldehyde have been reported so far. Katryniok et al. [8] reported silica supported heteropolyacids for the catalytic decarbonylation of LA to acetaldehyde, achieving 81-83% yield of acetaldehyde. More recently, we have reported metal sulfates and aluminate phosphate as catalysts for the decarbonylation of LA to acetaldehyde [32,33]. However, to my knowledge, magnesium aluminum oxides have not been used to catalyze decarbonylation of LA to acetaldehyde so far.



Magnesium aluminum oxides have attracted great interest in academy and industry due to its unique properties such as high resistance to chemicals, good mechanical strength in wide range of temperatures, low dielectric constant, excellent optical properties, low thermal expansion and good catalytic performances [34–41]. Several preparation methods such as hydrothermal techniques, sol-gel, spray plasma, cool drying, controlled hydrolysis, co-precipitation and aerosol method have been developed to synthesize magnesium aluminum oxides [36,41-44]. Among these methods, co-precipitation is viewed as a simple method to synthesize magnesium aluminum oxides. Due to excellent properties, magnesium aluminum oxides are widely used for optical engineering applications, electronic humidity sensors, integrated electronic devices, aluminum electronic cells and adsorbents [43]. Besides, its low acidity and thermal stability made magnesium aluminum oxide using as an excellent catalyst or catalyst support for oxidation of SO_2 to SO_3 [45], selective catalytic reduction of NO [46]. water-gas shift reaction [47], and propane dehydrogenation [48].

In this work, magnesium aluminum oxides with different structures were prepared, and used as a catalyst for decarbonylation of LA into acetaldehyde. Effect of pH values, calcination temperatures and Mg/Al molar ratios on formation of magnesium aluminum oxides was investigated. Based on these, we further discussed the relationship between preparation conditions for magnesium aluminum oxides and catalytic performances.

2. Experimental section

2.1. Materials

Lactic acid (analytic grade, 85–90 wt%) is obtained from Chengdu Kelong Chemical Reagent Co. and is used for the decarbonylation reaction of LA without further purification. Triple-distilled water is prepared in the laboratory and used to dilute lactic acid for required concentration. Aluminum nitrate (Al(NO₃)₃·9H₂O), magnesium nitrate (Mg(NO₃)₂·6H₂O), ammonia solution (25–28 wt%), acetaldehyde, acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and n-butanol, together with hydroquinone are purchased from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and acetaldehyde are used for gas chromatograph reference materials, and n-butanol is utilized as an internal standard material. Hydroquinone (0.3 wt%) is used as a polymerization inhibitor.

2.2. Preparation of catalysts

According to previous reports [40,43], magnesium aluminum oxides are prepared with a co-precipitation method. In a typical experiment, $5.0 \text{ g Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 14.6 g $Al(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg/Al molar ratio = 1:2) are fully dissolved in 100 mL distilled water under a stirring state for 1 h at room temperature. Next, the resultant solution is adjusted to different pH values (ca. pH = 7–8, 8–9, 10–11, >11) to form a white precipitate by dropwise addition of ammonium hydroxide solution (25 wt%). The resulting precipitate is filtered, completely rinsed with distilled water and dried at 120 °C for around 5 h. Besides other magnesium aluminum oxides with different Mg/Al molar ratios are also prepared with a similar method. Prior to use, the catalyst is calcined at demanded temperature in air for 6 h.

2.3. Catalyst characterization

Powder X-ray diffraction measurement is conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu Ka radiation. The FTIR spectra of the catalysts are recorded in

the range of 500–4000 cm⁻¹ on a Nicolet 6700 spectrometer. The morphologic features of the catalysts are examined by scanning electron microscope (SEM, JSM-6510) (shown in Fig. S1). The specific surface areas of catalysts are measured through nitrogen adsorption at 77 K using Autosorb IQ instrument. Prior to adsorption, the samples were treated at 250 °C under vacuum for 6 h and the specific surface area was calculated according to the Bru nauer-Emmett-Teller (BET) method. Pore size of catalysts is calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model. Surface acid and base properties of the samples are estimated by NH₃-TPD and CO₂-TPD, respectively, on a Quantachrome Instrument. The sample (ca. 50-60 mg) is purged with dry Ar (50 mL/min, purity >99.999 v_t %) at 500 °C for 1.0 h, followed by reducing the furnace temperature to 80 °C, and switching to a flow of $8v_t$ % NH₃/Ar or $10v_t$ % CO₂/Ar for 1 h to execute NH₃ or CO₂ adsorption. Then, NH₃ or CO₂ adsorbed on the sample is desorbed in the range of 80–700 °C at a rate of 10 °C/min.

2.4. Catalyst evaluation

The synthesis of acetaldehyde from LA over the catalysts is carried out in a fixed-bed quartz reactor with an 4 mm inner diameter operated at atmospheric pressure. The catalyst (ca. 0.3 g, 20-40 meshes) is placed in the middle of the reactor and quartz wool is placed in both ends. Firstly, the catalyst is pretreated at the required reaction temperature (ca. 380 $^\circ\text{C})$ for 1.0 h under N_2 with high purity (0.1 MPa, 1.0 mL/min). The feedstock (20 wt% solution of LA) is then pumped into the reactor (LA aqueous solution flow rate, 1.0 mL/h) and driven through the catalyst bed by nitrogen. The contact time of reactant over the catalyst is around 0.5 s, and the contact time is estimated according to Eq. (1) [32,49]. The liquid products are condensed using ice-water bath and analyzed off-line using a SP-6890 gas chromatograph with a FFAP capillary column connected to a FID. Quantitative analysis of the products is carried out by the internal standard method using *n*-butanol as the internal standard material. GC-MS analyses of the samples are performed using Agilent 5973N Mass Selective Detector attachment. The reaction tail gas is analyzed using GC with a packed column of TDX-01 connected to TCD detector. The conversion of LA and the selectivity toward acetaldehyde or other by-products are calculated according to Eqs. (2) and (3).

$$t_{C} = \frac{3600 \times 273.15 \times V_{\text{cat.}}}{22,400 \times (n_{\text{LA}} + n_{\text{H}_{2}0} + n_{C}) \times T}$$
(1)

 t_C : contact time (s); $V_{\text{cat.}}$: catalyst volume (mL); n_{LA} : the moles of lactic acid passed per hour; $n_{(\text{H2O})}$: the moles of water in lactic acid aqueous solution feed passed per hour; n_C : the moles of carrier gas passed per hour; T: reaction temperature (K).

Conversion (%) =
$$\frac{n_0 - n_1}{n_0} \times 100$$
 (2)

Selectivity (%) =
$$\frac{n_p}{n_0 - n_1} \times 100$$
 (3)

where n_0 is the molar quantity of LA fed into reactor, n_1 is the molar quantity of LA in the effluent, and n_p is the molar quantity of lactic acid converted to acetaldehyde or other byproducts such as propionic acid, acrylic acid, acetic acid, 2,3-pentanedione.

Area-specific catalytic rate is defined as previous references reported [50,51], and is determined with Eqs. (4) and (5).

LA Consumption rate

 $= \frac{amount \text{ of LA consumed per hour in the reactor } (mmol/h)}{surface \text{ area of catalyst in the reactor } (m^2)}$

 $(\mathbf{4})$

(5)

AD formation rate

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= \frac{amount \text{ of AD formed per hour in the reactor } (mmol/h)}{surface area of catalyst in the reactor } (m^2)
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3. Results and discussion

3.1. Characterization

3.1.1. BET

As for heterogeneous catalyst, its surface area is an important factor due to the catalytic reaction occurred on the surface [18,52–54]. In this section, effect of preparation parameters such as pH values, calcination temperatures and Mg/Al molar ratios on the specific surface, pore volume and pore distribution of the catalysts was investigated with nitrogen adsorption-desorption at 77 K using Autosorb IQ instrument, and the results were depicted in Tables 1-3 and Figs. S2-S4. From the BET data given in Table 1, the specific surface of magnesium aluminum oxides decreases with an increase of pH values except for the sample prepared at pH = 8–9. For example, the specific surface is $63.8 \text{ m}^2/\text{g}$ at pH = 7–8, while it decreases to 46.4 m^2/g at pH > 11. As for the pore size of sample, it increases with an increase of pH values. For instance, the pore diameter of the sample at pH = 7-8 is low, only 13.1 nm, but it increases to 34.4 nm at pH > 11. Table 2 shows effect of calcination temperature on sample physical properties

Table 1

BET data of magnesium aluminum oxides at different pH values.^a

pH value	$S_{\text{BET}}(m^2/g)$	Vol (cm ³ /g)	Pore size ^b (nm)
7–8	63.8	0.32	13.1
8-9	44.4	0.40	24.2
10-11	51.3	0.40	24.3
>11	46.4	0.34	34.4

^a Mg/Al molar ratio = 1:2, catalyst calcined at 1000 °C.

^b Calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model.

Table 2

BET data of magnesium aluminum oxides at different calcination temperatures.^a

Calcination temperature (°C)	$S_{\rm BET}~(m^2/g)$	Vol (cm ³ /g)	Pore size ^b (nm)
550	224.1	0.33	4.7
750	114.0	0.35	8.1
900	84.8	0.38	13.1
1000	63.8	0.32	13.1
1200	3.2	0.40	61.2

^a Mg/Al molar ratio = 1:2, pH, 7–8.

^b Calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model.

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BET data of magnesium aluminum oxides at different Mg/Al molar ratios.

Mg/Al	$S_{\text{BET}}(m^2/g)$	Vol (cm ³ /g)	Pore size ^b (nm)
MgO	16.4	0.24	2.9
1:1	55.1	0.37	24.2
1:2	63.8	0.32	13.1
1:3	64.1	0.29	13.1
1:6	62.0	0.20	10.0
1:8	53.2	0.19	9.0
Al_2O_3	38.7	0.21	10.0

^a Calcination temperature: 1000 °C, pH, 7-8.

^b Calculated from desorption branch data on the Barrett–Joyner–Halenda (BJH) model.

such as specific surface area, pore volume and pore size. The specific surface area of sample is very sensitive to calcination temperature. The specific surface area of sample drastically reduces with an increase of calcination temperature (ca. 224.1 m²/g at 550 °C and 3.2 m²/g at 1200 °C). Similar results on Mg–Al–O composites were reported by previous references [41]. Contrary to the specific surface area, pore diameter of sample rapidly increases with an increase of calcination temperature. Table 3 shows physical properties of magnesium aluminum oxides with different Mg/Al molar ratios together with pure MgO and Al₂O₃. It is clearly observed that all magnesium aluminum oxides have a higher specific surface area than pure samples MgO (16.4 m^2/g) or Al₂O₃ (38.7 m^2/g). This indicates that new species can form from a mixture including Mg and Al precursors calcined at high temperature such as 1000 °C. Apart from MgO (ca. 2.9 nm) and the magnesium aluminum oxide with Mg/Al = 1:1 (ca. 24.2 nm), the pore sizes for other samples are close to each other, distributing between 9 nm and 13.1 nm.

3.1.2. XRD and FT-IR

Fig. 1A shows the XRD patterns of Mg-Al-O composites prepared at different pH values. It is obvious that the magnesium aluminum oxide with pH = 7-8 displays the different characteristic diffraction peaks compared to other samples. The sample with pH = 7–8 well matches with the standard magnesium aluminum oxide (Mg_{0.388}Al_{2.408}O₄, PDF#48-0528); and it exhibits strong characteristic diffraction peaks at 19.2°, 31.6°, 37.3°, 45.4°, 56.5°, 60.2° and 66.3°, which can be indexed to (111), (220), (311), (400), (422), (511) and (440) diffractions, respectively. Other samples match well with the standard spinel (MgAl₂O₄, PDF#21-1152); and display strong characteristic diffraction peaks at 19.2°, 31.4°, 37.0°, 44.9°, 59.4° and 65.5°, which can be ascribed to (111), (220), (311), (400), (511) and (440) diffractions, respectively. This result suggests that pH values have an important influence in the formation of magnesium aluminum oxides. Fig. 1B depicted effect of calcination temperature on the formation of Mg-Al-O composite $(Mg_{0.388}Al_{2.408}O_4)$. When the calcination temperature is relatively lower, only 550 °C, we can observe the formation of $Mg_{0.388}Al_{2.408}O_4$. But it exhibits low characteristic diffraction peaks, indicating a low crystallinity for Mg_{0.388}Al_{2.408}O₄. When the calcination temperatures enhanced from 550 °C to 1000 °C, the characteristic diffraction peaks for Mg_{0.388}Al_{2.408}O₄ gradually increased, suggesting an increase of the crystallinity with an increase of calcination temperatures. As the calcination temperatures further increased (ca. 1200 °C), new diffraction peaks occurred, indicating that the structure of Mg_{0.388}Al_{2.408}O₄ encountered damage, and some converted other new species. Fig. 1C shows XRD patterns of magnesium aluminum oxides with Mg/Al molar ratios as well as pure MgO and Al_2O_3 . The Mg-Al-O composite with Mg/Al = 1 exhibited different diffraction peaks compared to other samples, and it matched well with the standard spinel (MgAl₂O₄, PDF#21-1152). It is known that pH value in synthetic conditions for MgAl₂O₄ spinel is around 9 [40–43]. However, the Mg–Al–O composites were prepared at pH = 7–8, lower than that prepared for MgAl₂O₄ spinel. We also note that solubility product constant for Al(OH)₃ (4.57×10^{-33}) is far less than that of Mg(OH)₂ (1.82×10^{-11}) . It happened that high concentration of Mg precursor compensated low pH value in the process of co-precipitation using ammonia water as a precipitant. Thus MgAl₂O₄ spinel was obtained at Mg/Al = 1. At the same time, a small quantity of MgO also existed in Mg-Al-O composite. When Mg/Al molar ratio increased to 2, pure Mg_{0.388}Al_{2.408}O₄ was formed. With further increase of Mg/Al molar ratios, Al₂O₃ content gradually increased in the samples.

In order to obtain information on the functional groups in the prepared samples, IR analyses were carried out as shown in Fig. 2A–C. From IR spectra of samples shown in Fig. 2A, three





Fig. 1. XRD of magnesium aluminate composites (A) prepared at different pHs, (B) prepared at different calcination temperatures and (C) prepared with different Mg/Al molar ratios. Conditions: (A), Mg/Al molar ratio = 1:2, catalyst calcined at 1000 °C; (B), pH, 7–8, Mg/Al molar ratio = 1:2; (C), pH, 7–8, catalyst calcined at 1000 °C.

Fig. 2. FT-IR of magnesium aluminate composites (A) prepared at different pH values, (B) prepared at different calcination temperatures and (C) prepared with different Mg/Al molar ratios. Conditions: (A), Mg/Al molar ratio = 1:2, catalyst calcined at 1000 °C; (B), pH, 7–8, Mg/Al molar ratio = 1:2; (C), pH, 7–8, catalyst calcined at 1000 °C.



Fig. 3. TPD profiles of magnesium aluminum oxides (A) NH₃-TPD of magnesium aluminum oxides prepared with different pH values and (B) corresponding CO₂-TPD; (C) NH₃-TPD of magnesium aluminum oxides prepared at different calcination temperatures and (D) corresponding CO₂-TPD; (E) NH₃-TPD of magnesium aluminum oxides prepared with different Mg/Al molar ratios together with pure MgO and Al₂O₃ and (F) corresponding CO₂-TPD.

samples prepared at pH > 8 are almost identical. Absorption bands of around 3440 cm⁻¹ and 1630 cm⁻¹ are assigned to OH and adsorption H₂O, respectively [38,41,42]. Besides, the IR spectra of these three samples exhibit two characteristic frequencies at ca. 533 cm⁻¹ and 700 cm⁻¹ attributing to [AlO₆] groups and the lattice vibration of Mg–O stretching, indicating an existence of MgAl₂O₄ spinel structure in the samples [42]. The sample prepared at pH = 7–8 displays slightly different IR spectra in range of 500– 900 cm⁻¹, suggesting that the structure of Mg–Al–O composite (Mg_{0.388}Al_{2.408}O₄) obtained at pH = 7–8 is different from other samples (MgAl₂O₄). This result accords with the aforementioned XRD characterization. Fig. 2B shows the IR spectra of the samples calcined at different temperatures. When the calcination temperature is below 1000 °C, IR spectra for theses samples are almost constant except that the intensities for absorption bands are different from each other. However as the calcination temperature further increases from 1000 °C to 1200 °C, a drastical change takes place in the IR spectra. This result is also in concert with that obtained from XRD characterization in Fig. 1B. From IR spectra of the samples with different Mg/Al molar ratios shown in Fig. 2C, the weak absorption band at 819 cm⁻¹ for the sample with Mg/Al molar ratio = 1 obviously disappears in comparison with the sample with Mg/Al molar ratio = 2, indicating a difference in their molecular structures.

3.1.3. NH₃-TPD/CO₂-TPD of Mg-Al-O composites

Fig. 3A-F shows the NH₃-TPD profiles of the as-prepared samples varving pH values, calcination temperatures and Mg/Al molar ratios together with corresponding CO₂-TPD profiles. In Fig. 3A and B, the sample with pH = 7-8 displayed a broad desorption peak in the region of 150-300 °C in which were regarded as weak-medium acidity (alkalinity), and was different in TPD curves from others obtained at pH > 8. The peak centered at around 200 °C for other samples splits into two peaks, suggesting that acidity (alkalinity) increased with an increase of pH values. From the profiles shown in Fig. 3C and D, desorption peak at around 400 °C characterized medium-strong acidity (alkalinity) moved to the region in low temperatures as calcination temperature increased, indicating that acidity (alkalinity) for samples decreased. It is noteworthy that the desorption peaks of the sample almost disappeared when the calcination temperature further increased to 1200 °C. These indicated that both acidity and alkalinity for the sample calcined at 1200 °C became the weakest.

Fig. 3E and F shows the TPD profiles for Mg-Al-O composites with different ratios as well as pure Al₂O₃ and MgO, respectively. By comparing the NH₃-TPD curve of MgO with corresponding CO₂-TPD curve, it is found that they exhibit double peaks at 250 °C and 400 °C, and the high temperature desorption peak for the former is higher than the latter. This result suggests that acidity-alkalinity balance does not exist on the surface of MgO. Through further observation for CO₂-TPD curve for MgO, it is easily found that weak alkalinity sites are more abundant than strong alkalinity sites on the surface of MgO. As for pure Al₂O₃, a broad and slight desorption peak at 450 °C occurs in Fig. 3E except for the peak at 200 °C, suggesting that weak acidity sites as well as medium strong acidity sites exist on the surface of pure Al₂O₃. Observing the CO₂-TPD curves shown in Fig. 3F, pure Al₂O₃ displays only a desorption peak at 200 °C. All the Mg-Al-O composites with different Mg/Al molar ratios except for the sample with Mg/Al = 1 exhibit a broad desorption peak in low temperature region (150-300 °C), suggesting that weak and medium acidity (alkalinity) sites exist on the surface of the samples. In addition, the intensity of desorption peak is slightly different from each other, indicating that the number of weak and medium acidity (alkalinity) sites is also different from each other.

3.2. Catalyst evaluation

3.2.1. Effect of catalyst preparation means on the catalytic performance

3.2.1.1. pH values. Catalytic reactions for gas phase decarbonylation of LA over Mg–Al–O composites were performed at 380 °C with LA concentration (20 wt%) and feed flow rate (1 mL/h), and the results were shown in Fig. 4A and B and Table 4. It is clearly seen from Fig. 4A that LA conversion is drastically influenced by pH values. For example, LA conversion decreases with an increase of pH values. Based on the effect of TOS (time on stream) on LA conversion at different pH values, different catalysts display evidently



Fig. 4. Performance of magnesium aluminum oxides at different pHs by the time course of LA conversion (A) and acetaldehyde selectivity (B). (a) Catalyst volume, 0.38 mL, magnesium aluminum oxides prepared through Mg(NO₃)₂ and Al(NO₃)₃ as precursors at calcination temperature of 1000 °C, reaction temperature, 380 °C, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water. (b) LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

Table	4	
Effect	of pH	values.ª

pН	LA conv. (%)	Sel. (%	6) ^b			Area-specific catalytic rate (mmol $h^{-1} m^{-2}$)			
		AD	PA	ACA	AA	PD	LA consumption	AD formation	
7-8	100	91.4	2.6	2.2	2.6	0.9	878.1	802.6	
8-9	79.1	90.2	3.1	1.9	2.7	1.1	963.6	869.2	
10-	11	78.7					88.6	3.8	
		1.1					859.4	761.5	
2.0	4.3								
>11	67.9	83.4	6.4	2.5	6.1	1.5	819.8	683.7	

^a Catalyst, 0.38 mL, 0.28–0.29 g; magnesium aluminum oxides prepared through Mg(NO₃)₂ and Al(NO₃)₃ as precursors at calcination temperature of 1000 °C; reaction temperature, 380 °C; particle size, 20–40 meshes; carrier gas N₂, 1 mL/min; feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water; TOS, 4–6 h.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

different stabilities. It is noted that the Mg–Al–O composite prepared at pH = 7 offers an excellent stability. For example, LA was almost fully converted on the whole time (TOS, 1–8 h). However LA conversions over other Mg-Al-O composites prepared at pH > 8 drastically decreased as the time on stream lengthened. From the results shown in Fig. 4B, similar experimental phenomena were observed except for the Mg-Al-O composite prepared at pH = 8-9. AD selectivity decreased with an increase of pH values. Furthermore, AD selectivity over all the Mg-Al-O composite catalysts slightly fluctuated with a change in reaction time. In addition, as an important method characterized catalytic performance, area-specific catalytic rates were calculated at TOS = 4–6 h (depicted in Table 4). We can easily observe that area-specific catalytic rate decreased with an increase of pH values except for the Mg–Al–O composite prepared at pH = 7-8. It is noteworthy that LA conversion over the Mg-Al-O composite catalyst prepared at pH = 7–8 attains 100%. It is likely that some of the catalyst surface was not utilized. However the area-specific catalytic rate for these catalysts was determined based on the total surface of the catalyst. Thus the catalyst prepared at pH = 7-8 displayed lower area-specific catalytic rate ostensibly. In fact, it can display higher area-specific catalytic rate (confirmed by the following Section 3.2.2.3 Effect of LA LHSV). According to XRD and FTIR characterizations shown in Figs. 1A and 2A, we found that the Mg-Al-O composite obtained at pH = 7-8 belongs to $Mg_{0.388}Al_{2.408}O_4$, while Mg–Al–O composites obtained at other pH values ascribe to spinel $(MgAl_2O_4)$. Besides, $Mg_{0.388}Al_{2.408}O_4$ (63.8 m²/g) has bigger specific surface area than other spinels $(44.4-51.3 \text{ m}^2/\text{g})$. It is known that as for heterogeneous catalysts, bigger specific surface area favors to the catalytic reaction. Thus it is not astonishing that the highest LA conversion over the Mg–Al–O composite at pH = 7-8 was achieved. In addition, decarbonylation of LA to acetaldehyde catalyzed by weak-medium acid has been recognized by previous reports [32,33]. Through NH₃-TPD characterization for Mg-Al-O composites with different pH values, the Mg-Al-O composite $(Mg_{0.388}Al_{2.408}O_4)$ with pH = 7–8 displays a broad desorption peak in the region of 150-300 °C in which were regarded as weak-medium acidity, and is different in TPD curves from others obtained at pH > 8. The peak centered at around 200 °C for other samples splits into two peaks, suggesting that acidity increases with an increase of pH values. With respect to the acidity of the catalysts, the Mg–Al–O composite (Mg_{0.388}Al_{2.408}O₄) with pH = 7-8 has more appropriate acidity compared to others for decarbonylation of LA to acetaldehyde. Considering the specific surface area and acidity of catalysts, the Mg-Al-O composite ($Mg_{0.388}Al_{2.408}O_4$) obtained at pH = 7–8 is a potentially excellent catalyst for gas phase decarbonylation of LA to acetaldehyde.

3.2.1.2. Mg/Al molar ratio. Fig. 5 and Table 5 show the catalytic performance of Mg-Al-O composites with different Mg/Al molar ratios as well as pure MgO and Al₂O₃. From Fig. 5A, time on stream had an important influence in LA conversion over some catalysts such as Mg-Al-O composites with Mg/Al = 1:6 and 1:8, respectively, pure Al₂O₃ and MgO. For these catalysts except for pure MgO, they displayed an excellent initial activity, while as time on stream lengthened the activity (LA conversion) drastically decreased. Interestingly, with an increase of Mg/Al molar ratios the catalyst displayed better activity and stability. For example, LA conversion maintained 100% on the whole reaction time (TOS: 0-8 h) over the catalyst with Mg/Al = 1:2. However with further increase of Mg/Al molar ratios (ca. Mg/Al = 1:1), the catalyst offered lower LA conversion (ca. 70-81%) although the catalyst yet remained better stability. Unlike effect of time on stream on LA conversion, it has a slight influence in acetaldehyde selectivity (shown in Fig. 5B). Pure MgO (AD sel.: 65-70%) displayed less acetaldehyde selectivity compared to other catalysts (AD Sel.: 87–92%). From the data obtained at TOS = 6-8 h shown in Table 5, area-specific catalytic rate changed with Mg/Al molar



Fig. 5. Performance of magnesium aluminum oxides together with MgO and Al₂O₃ by the time course of LA conversion (A) and acetaldehyde selectivity (B).

Table 5Effect of Mg/Al molar ratio.a

Mg/ LA conv. Sel. (%) ^b Area-specific cata Al (%) rate (mmol h ⁻¹ m)	llytic 1 ⁻²) D
	D
AD PA ACA AA PD LA A consumption for	rmation
MgO 12.9 69.9 13.6 8.9 6.0 1.3 725.8 5 1:1 80.7 89.9 3.3 2.2 3.5 1.0 792.2 7 1:2 100 91.4 2.6 2.2 2.6 0.9 878.1 8 1:3 89.4 90.3 2.3 3.4 2.7 1.0 729.3 6 1:6 74.3 87.7 3.7 3.5 3.6 1.2 587.4 5 1:8 82.1 89.2 2.5 4.1 3.0 1.0 756.5 6 Al ₂ O ₃ 70.3 91.2 2.7 2.7 2.3 0.9 863.5 7	07.3 12.2 02.6 58.5 15.2 74.8 87.5

^a Catalyst, 0.38 mL, MgO, 0.17 g, Al₂O₃, 0.33 g, magnesium aluminum oxides prepared through Mg(NO₃)₂ and Al(NO₃)₃ as precursors at calcination temperature of 1000 °C, 0.30–0.32 g, pH, 7–8, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water, reaction temperature: 380 °C.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

ratios. The fastest area-specific catalytic rate (LA consumption: 878.1 mmol $h^{-1} m^{-2}$ and AD formation: 802.6 mmol $h^{-1} m^{-2}$) was achieved over the Mg–Al–O composite with Mg/Al = 1:2. As discussed above (shown in Fig. 1C), the Mg–Al–O composite obtained at Mg/Al = 1:2 is attributed to Mg_{0.388}Al_{2.408}O₄ with high purity. When the Mg/Al molar ratio (ca. 1:1) is higher than 1:2, the

Mg–Al–O composite obtained is attributed to MgAl₂O₄ spinel. While the Mg/Al molar ratio is lower than 1:2, the mixture including $Mg_{0.388}Al_{2.408}O_4$ and Al_2O_3 is obtained. It is known from the discussion in Section 3.2.1.1 that $Mg_{0.388}Al_{2.408}O_4$ has more excellent activity due to appropriate acidity sites on its surface.

3.2.1.3. Calcination temperature. Fig. 6 and Table 6 show effect of calcination temperature on the performance of catalysts. LA conversion increased from 75.9% to 100% as the calcination temperature increased from 550 °C to 750 °C. Subsequently, LA conversion remained constant (100%) in the range between 750 °C and 1000 °C. But LA conversion drastically decreased with further increase of calcination temperature. For example, 24.3% of LA conversion was achieved at 1200 °C of calcination temperature. Although area-specific catalytic rate (LA consumption: 2247.5 mmol $h^{-1} m^{-2}$ and AD formation: 1613.7 mmol $h^{-1} m^{-2}$) on the catalyst calcined at 1200 °C was the highest among all the catalysts calcined at different temperatures (ca. 550-1200 °C), LA conversion as well as acetaldehyde selectivity is the lowest due to its low specific surface area (only $3.2 \text{ m}^2/\text{g}$ far lower than others $(63.8-224.1 \text{ m}^2/\text{g})$). In order to better understand the effect of calcination temperature on the catalytic performance, we can draw support from the XRD characterization shown in Fig. 3B. With an increase of calcination temperature, characteristic diffraction peaks for Mg0.388Al2.408O4 also gradually increased, suggesting that



Fig. 6. Performance of magnesium aluminum oxides calcined at different temperatures by the time course of LA conversion (A) and acetaldehyde selectivity (B).

high temperature favored the formation of $Mg_{0.388}Al_{2.408}O_4$. Furthermore $Mg_{0.388}Al_{2.408}O_4$ was vied as active species. Thus with an increase of calcination temperature, the catalytic performance became better and better. Unfortunately, LA conversion drastically decreased to 24.3% as calcinations temperature increased to 1200 °C. But it is not surprising that under the calcination temperature of 1200 °C the catalyst partly decomposed or transformed to other species. In addition, similar to LA conversion, acetaldehyde selectivity slightly fluctuated within 750–1000 °C. This can be explained using $Mg_{0.388}Al_{2.408}O_4$ selectively catalyzed decarbonylation of LA into acetaldehyde.

3.2.2. Reaction conditions

3.2.2.1. Reaction temperature. According to the discussion on preparation conditions of catalysts in the preceding sections, we obtained the optimal preparation conditions for Mg0 388Al2 408O4 (pH, 7–8: calcination temperature, 1000 °C: Mg/Al molar ratio, 1:2.). Next, effect of reaction conditions on the decarbonylation of LA would be investigated. As an important factor determining the reaction rate and reaction selectivity, reaction temperature was firstly discussed [55,56]. From effect of reaction temperature on decarbonylation of LA shown in Fig. S5A, LA conversion increased with an increase of reaction temperature from 320 °C to 380 °C. For a fixed catalyst, area-specific catalytic rate also increases with an increase of reaction temperature. For this reason, LA conversion increased with an increase of reaction temperature. However as the reaction temperature increased to 400 °C, LA conversion rapidly reduced at 2-6 h on stream. Interestingly, area-specific catalytic rate at 400 °C also decreased compared to the data obtained at 360 °C or 380 °C, indicating part deactivation of catalyst active sites. As for acetaldehyde selectivity (shown in Table 7), it slightly decreased with an increase of reaction temperature. Besides, from correlation between TOS and acetaldehyde selectivity depicted in Fig. S5B, it is clearly seen that acetaldehyde selectivity was slightly influenced by TOS.

3.2.2.2. LA concentration. Effect of LA concentration on the reaction performance was also investigated over Mg_{0.388}Al_{2.408}O₄ at 380 °C and the results were given in Table 8. Notably, unlike the results obtained over $Al_2(SO_4)_3$ catalyst [32], acetaldehyde selectivity was hardly influenced, whereas LA conversion was influenced with change of LA concentration. LA was completely converted when LA concentration was lower than 20 wt%. But a residue of LA began to occur as LA concentration was more than 30 wt%. As for most of by-products such as propionic acid, acetic acid and acrylic acid, the selectivity fluctuated with an increase of LA concentration. But 2,3-pentanedione selectivity regularly enhanced with an increase of LA concentration. It is known that formation of 2,3-pentanedione is via a Claisen condensation reaction of two lactate moieties followed by decarboxylation and dehydration steps [24,54]. Thus higher LA concentration favors its condensation reaction to form 2,3-pentanedione. However, the selectivity of 2,3-pentanedione was far lower compared to other by-products. This suggested that apart from LA concentration factor, acid-base properties play an important role for catalytic formation of 2,3-pentanedione [24,25,52]. According to CO₂-TPD characterization shown in Fig. 3B, only a desorption peak occurred at low temperature, indicating that weak alkalinity existed on the catalyst surface. Therefore, low selectivity of 2,3-pentanedione was obtained on Mg_{0 388}Al_{2 408}O₄ catalyst at 380 °C.

3.2.2.3. Liquid hourly space velocity (LHSV). LHSV is generally used to evaluate the performance of heterogeneous catalyst [53,57,58]. Table 9 shows the influence of LA LHSV on reaction performance. The reaction was conducted at 380 °C with LA flow rate changed from 0.5 to 10 mL/h (corresponding LHSV = $1.3-26.3 h^{-1}$). For LA

Table	6	
Effect	of calcination	temperature. ^a

Calcination temperature (°C)	LA conv. (%)	Sel. (%) ^b					Area-specific catalytic rate $(\text{mmol } h^{-1} m^{-2})$		
		AD	PA	ACA	AA	PD	LA consumption	AD formation	
550	75.9	83.5	5.0	5.3	4.2	1.7	166.0	138.6	
750	100	88.4	3.0	4.7	2.7	1.0	443.9	392.4	
900	100	91.0	2.4	3.3	2.2	0.9	616.6	561.1	
1000	100	91.4	2.6	2.2	2.6	0.9	878.1	802.6	
1200	24.3	71.8	12.7	4.7	6.5	4.0	2247.5	1613.7	

^a Mg_{0.38}Al_{2.4}O₄ catalyst, 0.38 mL, Mg/Al molar ratio = 1:2, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water, reaction temperature: 380 °C, TOS: 6–8 h.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

Table '	7
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Effect of reaction temperature.^a

Reaction temperature (°C)	LA conv. (%)	Sel. (%) ^b	Sel. (%) ^b				Area-specific catalytic rate (mmol $h^{-1} m^{-2}$)		
		AD	PA	ACA	AA	PD	LA consumption	AD formation	
320	54.7	93.7	1.2	1.9	2.6	0.3	437.4	409.9	
340	82.3	93.5	1.4	1.5	2.5	0.9	670.1	626.6	
360	91.9	92.0	1.9	1.8	3.0	1.0	776.5	714.4	
380	100	91.4	2.6	2.2	2.6	0.9	878.1	802.6	
400	80.0	90.1	2.8	2.5	2.0	0.9	716.5	645.6	

^a Mg_{0.38}Al_{2.4}O₄ catalyst, 0.38 mL, 0.28 g, Mg/Al molar ratio = 1:2, pH = 7–8, catalyst calcination temperature, 1000 °C, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, LA feedstock: 20 wt% in water, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water, TOS: 6–8 h.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

Table 8

Effect of LA concentration. ^a	fect of LA concentration. ^a									
LA concentration (wt%)	LA conv. (%)	Sel. (%) ^b					Area-specific catalytic rate $(mmol h^{-1} m^{-2})$			
		AD	PA	ACA	AA	PD	LA consumption	AD formation		
10	100	91.2	2.2	4.0	1.5	0.6	476.4	434.5		
15	100	91.5	1.8	3.5	2.2	0.6	685.5	627.2		
20	100	91.7	2.5	2.6	2.0	0.8	878.1	805.2		
30	91.8	91.2	2.3	3.2	2.0	0.9	1081.9	986.7		
40	90.5	91.7	1.6	2.9	2.2	1.0	1286.6	1179.8		

^a Mg_{0.38}Al_{2.4}O₄ catalyst, 0.38 mL, 0.28–0.30 g, Mg/Al molar ratio = 1:2, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, feed flow rate: 1 mL/h, reaction temperature: 380 °C, TOS: 1–2 h.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

Table 9 Effect of LA LHSV.^a

LA solution LHSV (h^{-1})	LA conv. (%)	Sel. (%) ^b					Area-specific catalytic rate $(mmol h^{-1} m^{-2})$	
		AD	PA	ACA	AA	PD	LA consumption	AD formation
1.3	100	89.0	4.0	3.2	2.1	1.4	228.5	203.4
2.6	100	91.7	2.5	2.6	2.0	0.9	878.1	805.2
3.9	100	92.1	1.9	2.3	2.7	0.6	1919.3	1767.6
5.2	100	91.9	1.8	2.2	3.2	0.6	3317.2	3048.5
8.4	100	93.2	1.5	1.8	2.1	0.9	7463.8	6956.3
13.0	97.2	94.0	1.3	1.3	2.4	0.7	19785.9	18598.7
20.8	88.5	95.0	0.9	1.3	2.0	0.4	45294.6	43029.9
26.3	82.9	95.1	0.9	1.4	2.0	0.2	74249.9	70611.6

^a Mg_{0.38}Al_{2.4}O₄ catalyst, 0.38 mL, 0.29–0.30 g, Mg/Al molar ratio = 1:2, particle size: 20–40 meshes, carrier gas N₂: 1 mL/min, LA feedstock: 20 wt% in water, reaction temperature: 380 °C, TOS: 1–2 h.

^b LA: lactic acid, AD: acetaldehyde, PA: propionic acid, ACA: acetic acid, AA: acrylic acid, PD: 2,3-pentanedione.

conversion, it almost remained at 100% when LA LHSV was lower than 8.4 h⁻¹. As LA LHSV increased from 8.4 h⁻¹ to 26.3 h⁻¹, LA conversion gradually decreased from 100% to 82.9%. Acetaldehyde selectivity, unlike LA conversion, increased slowly with an increase of LA LHSV. It is known that LA contact time on the surface of $Mg_{0.388}Al_{2.408}O_4$ catalyst shortens with the enhancement of LA LHSV. Enhancement of LA LHSV favored the selective

formation of acetaldehyde, indicating that decarbonylation reaction of LA is faster than other side reactions. Area-specific catalytic rate quickly increased with an increase of LA solution LHSV. For example, LA consumption rate was 228.5 mmol h^{-1} m⁻² at LA solution LHSV = 1.3 h^{-1} while it attained to 74249.9 mmol h^{-1} m⁻² at LA solution LHSV = 26.3 h^{-1} . For that reason, LA conversion (82.9%) was very high at high LHSV of 26.3 h^{-1} .

3.2.3. Correlation between the acid–base property and catalytic performance of Mg–Al–O composites

It has been known that the catalytic decarbonylation rate of LA into acetaldehyde over the calcium hydroxyapatite would be dependent on the catalyst surface acid-base property [50,59]. Indeed, from the results shown in Fig. 3A and B and Fig. 7, surface acid-base property of catalysts changes with pH values. It is noted that surface acidity and basicity depicted in Fig. 7 are determined only in the range of 150–300 °C of desorption temperatures, which favors decarbonylation reaction of LA [33]. An attempt is then made to correlate the rates of LA consumption and product AD formation with the surface acidity and basicity of catalysts prepared at different pH values, and the results were shown in Figs. 8 and 9. It is clear that LA consumption rate increased with increasing acid density apart from acid density of 1.2 umol/m² (corresponding pH = 7-8), but decreased with the surface base density. It seems that LA consumption rate (878.1 mmol $h^{-1} m^{-2}$) obtained at $1.2 \,\mu\text{mol/m}^2$ (corresponding pH = 7–8) is lower than others. Actually, LA consumption rate (74249.9 mmol h⁻¹ m⁻², corresponding LA conversion = 82.9% shown in Table 9) obtained at $1.2 \,\mu mol/m^2$ is two orders of magnitude faster than others $(819.8-963.6 \text{ mmol } h^{-1} \text{ m}^{-2}, \text{ corresponding LA conversion} = 67.9-$ 79.1% shown in Table 4). Similarly, AD formation rate also increased with increasing surface acid density but decreased with surface base density. The observations on the increase with surface acid density and decrease with base density of the area-specific catalytic rates for LA consumption and AD formation agreed well with the previous reports [33,50,51].

3.2.4. Catalyst stability

Long-term stability is a very important characteristic for a heterogeneous catalyst [55,56,60–62]. The catalytic stability of $Mg_{0.388}Al_{2.408}O_4$ was investigated at 380 °C and LA feed flow rate of 5 mL/h (corresponding LA LHSV = 13.0 h⁻¹), and the results were depicted in Fig. 10. LA conversion slowly gradually decreased with an increase of time on stream. For example, LA conversion reduced with only 25% (from 95% to 70%) within 400 h on stream. When the time on stream lengthened to 500 h, LA conversion still remained above 58%. More importantly, acetaldehyde selectivity almost remained constant (>93%) during the whole time on stream. To our great delight, so far this is the best result concerning LA conversion, acetaldehyde selectivity and LA LHSV. It is noted that for $Mg_{0.388}Al_{2.408}O_4$, LA LHSV is at least 5 times than previous reports [32,33]. Long-term stability as well as high selectivity of acetaldehyde is also related to catalyst acid–base balance. As mentioned



Fig. 7. Surface acidity and basicity of magnesium aluminum oxides prepared with different pH values.



Fig. 8. Dependences of the area-specific catalytic rate of LA consumption on the surface acidity and basicity of the magnesium aluminum oxides prepared with different pH values.



Fig. 9. Dependences of the area-specific catalytic rate of AD formation on the surface acidity and basicity of the magnesium aluminum oxides prepared with different pH values.



Fig. 10. Durability of $Mg_{0.388}Al_{2.408}O_4$ catalyst. Catalyst volume, 0.38 mL, 0.30 g, Mg/Al molar ratio = 1:2, particle size: 20–40 meshes, carrier gas N_2 : 1 mL/min, LA feedstock: 20 wt% in water, feed flow rate: 5 mL/h, reaction temperature: 380 C.

above, for $Mg_{0.388}Al_{2.408}O_4$ catalyst predominant weak-medium acidity as well as an excellent acid–base balance plays an important role in durability and acetaldehyde selectivity. It is known that strong acidic sites have a strong catalysis for decomposition of C–C bond, resulting in deposition of carbon or formation of coke on the catalyst surface [51,60,63]. Thus the catalyst with more strong acidic sites rapidly deactivates in the process of the catalytic decarbonylation reaction of LA due to covering the active sites of the catalyst surface by the formed carbon or cokes. But for $Mg_{0.388}Al_{2.408}O_4$ catalyst, it contains weak-medium acidity and remains an excellent acid–base balance. Furthermore, it lacks strong acidic sites on the catalyst surface. Therefore $Mg_{0.388}Al_{2.408}O_4$ catalyst offered an excellent performance including high selectivity and excellent stability.

3.3. Reaction mechanism

Unlike the mechanism on dehydration of LA into acrylic acid which has been discussed by many previous reports [50,51,59],

the mechanism for decarbonylation of LA to acetaldehyde is rarely investigated so far. Recently, Ghantani et al. [59] have proposed the decarbonylation reaction mechanism of LA to form acetaldehyde over the calcium hydroxyapatite. More recently, based on aluminum sulfate utilized as a catalyst we have also discussed the mechanism on decarbonylation of LA to acetaldehyde [32]. Similarly, based on the experimental results achieved over Mg_{0.388}Al_{2.408}O₄ catalyst, we proposed the possible reaction mechanism on formation of acetaldehyde from LA as followed in Scheme 1. Firstly, dissociative adsorption of LA occurs on Mg_{0.388}Al_{2.408}O₄ catalyst, where the hydroxyl group in LA molecule adsorbs on the Mg site, forming a C–O–Mg bond and the hydroxyl proton gets abstracted by aluminate oxygen forming Al-OH. Subsequently, Al–OH further reacts with the carboxylic –OH group to form aluminate ester. In the end, this aluminate ester decomposes to produce acetaldehvde and carbon monoxide. In addition, the possible mechanisms for the formation of acrylic acid and 2,3-pentanedione have also been proposed, and shown in Scheme 1 and Scheme 2 in Supporting Information.



Scheme 1. Proposed mechanism for acetaldehyde formation from LA over Mg_{0.388}Al_{2.408}O₄ catalyst.

4. Conclusions

Magnesium aluminum oxides prepared with co-precipitation method were firstly used to catalyze the decarbonylation of LA to acetaldehyde. Formation of magnesium aluminum oxides is very sensitive to pH values. Low pH values are favorable to the formation of Mg_{0.388}Al_{2.408}O₄ while high pH values are favorable to the formation of MgAl₂O₄ spinel. The crystallinity of Mg_{0.388}Al_{2.408}O₄ increases with an increase of calcination temperature in range of 550-1000 °C. Among magnesium aluminum oxides. Mg_{0.388}Al_{2.408}O₄ offers the best catalytic performance. For Mg_{0.388}Al_{2.408}O₄ catalyst, LA conversion increases drastically with an increase of reaction temperature while acetaldehyde selectivity decreases slowly. Effect of LA LHSV on reaction performance suggests that acetaldehyde selectivity increases with an increase of LA LHSV. Decarbonylation reaction of LA over Mg_{0.388}Al_{2.408}O₄ catalyst is not sensitive to LA concentrations. Under the optimal reaction conditions, the stability of Mg_{0.388}Al_{2.408}O₄ catalyst was evaluated at LA LHSV = $13.0 h^{-1}$. Encouragingly, LA conversion reduced with only 25% (from 95% to 70%) within 400 h on stream. More importantly, acetaldehyde selectivity almost remained constant (>93%) during the whole time on stream.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.05.016.

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