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Sustainable production of acetaldehyde from lactic acid over the magnesium aluminate spinel

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ABSTRACT

Magnesium aluminate spinel was prepared with co-precipitation method by varying Mg, Al precursors, Mg/Al molar ratios and calcination temperatures. The as-prepared magnesium aluminate spinel was characterized by nitrogen adsorption-desorption, XRD, FT-IR, NH₃-TPD, CO₂-TPD and SEM, and were employed to catalyse the vapour-phase decarbonylation of lactic acid (LA) to produce acetaldehyde. Among Mg, Al precursors investigated in our experiment, overwhelming majority can be easily transformed into spinel under high temperatures, which offered highly efficient catalytic performance for decarbonylation of LA to acetaldehyde. Mg/Al molar ratios had a significant influence for this reaction. Under high Mg/Al molar ratios, the catalyst displayed low selectivity to acetaldehyde and high selectivity to propionic acid due to strong alkalinity on its surface. Decreasing Mg/Al molar ratios favoured to acetaldehyde selectivity. Calcination temperatures evidently affected to form spinel structure. With enhancing calcination temperatures, it favoured to the formation of magnesium aluminate spinels, displaying a high crystallinity. Meanwhile, the catalytic performances became better with an increase of calcination temperatures. Accordingly, magnesium aluminate spinel was thought as active species for decarbonylation of LA to acetaldehyde. With further increase of calcination temperatures, the structure of magnesium aluminate spinel was destroyed. At the same time, the catalytic performance also drastically decreased. These results can further confirm the spinel as active species. Under the optimal reaction conditions, LA was almost converted and the selectivity of acetaldehyde achieved 87.5% over the magnesium aluminate spinel with Mg/Al molar ratio = 1:2 at calcination temperature of 1000 °C.

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1. Introduction

Magnesium aluminate spinel (MgAl₂O₄) has 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, adsorption properties and good catalytic performances [1–10]. Several preparation methods such as hydrothermal techniques [11,12], sol-gel [13,14], flame spray pyrolysis [15], cool drying [16,17], controlled hydrolysis [18], co-precipitation [5,19] and aerosol method [20,21] have been developed to synthesize magnesium aluminate spinels. Among these methods, co-precipitation is viewed as a simple method to synthesize spinel. Due to excellent properties, spinel is widely used for optical engineering applications, electronic humidity sensors, integrated electronic devices, aluminium electronic cells and adsorbents [10]. Besides, its low acidity and thermal stability made spinel an excellent catalyst or cat-

alyst support for oxidation of SO₂ to SO₃ [22], selective catalytic reduction of NO [23], water-gas shift reaction [24], and propane dehydrogenation [25].

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, butylene glycol, and chloral [26,27]. So far, acetaldehyde is mainly obtained from ethylene route using PdCl₂-CuCl₂ as a catalytic system [28]. Due to the increasing depletion of petroleum reserves which are used to produce ethylene via high temperature pyrolysis or catalytic cracking, this route will be restricted in the near future. For this reason, it has become a heated research that acetaldehyde, like other chemicals such as 5-hydroxymethylfurfural, 1-butanol and succinic acid, is produced from the biomass [29–36]. A case in point is that acetaldehyde is produced via catalytic dehydrogenation of ethanol or partial oxidation of ethanol [26,37–41]. Another case is that acetaldehyde is also obtained through decarbonylation of lactic acid (LA) [32]. As a crucial platform molecule, LA is utilized to produce many value added chemicals such as acrylic acid [42–46], acetaldehyde [32,47–48], 2,3-pentanedione [49,50], propionic acid [51], pyruvic acid [52] and polymers [53]. Except for corn starch, rich and inexpensive biomass

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materials such as cellulose [54], sugars [55], and sorbitol [56] 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. Katoryniok et al. [32] reported silica supported heteropolyacids for the catalytic decarbonylation of LA to acetaldehyde, achieving 81~83% yield of acetaldehyde at 275 °C. More recently, we have reported metal sulphates and aluminate phosphate as catalysts for the decarbonylation of LA to acetaldehyde [47,48]. However, to my knowledge, magnesium aluminate spinel has not been used to catalyse decarbonylation of LA to acetaldehyde to date.

In this work, we presented an efficient catalyst (MgAl_2O_4) for decarbonylation of LA into acetaldehyde. Effect of precursors, Mg/Al molar ratios and calcination temperatures on formation of spinel was investigated. Based on these, we further discussed the relationship between preparation conditions for spinel catalysts and catalytic performances.

2. Experimental section

2.1. Materials

Lactic acid (analytic grade, 85~90 wt%) was purchased from Chengdu Kelong Chemical Reagent Co. and was used for the synthesis of acetaldehyde without further purification. Triple-distilled water was prepared in the laboratory and was used to dilute lactic acid for demanded concentration. Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), magnesium sulphate ($\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$), magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium aluminate (NaAlO_2), aluminium isopropoxide ($\text{C}_9\text{H}_{21}\text{AlO}_3$), ammonia solution (25~28 wt%), acetaldehyde, acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and *n*-butanol, together with hydroquinone were purchased from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and acetaldehyde were used for gas chromatograph reference materials, and *n*-butanol was utilized as internal standard material. Hydroquinone (0.3 wt%) was used as a polymerization inhibitor.

2.2. Preparation of catalysts

According to previous reports [7,10,57], magnesium aluminate spinel was prepared with a co-precipitation method. In a typical experiment, 5.0 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 14.6 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg/Al molar ratio = 1:2) were fully dissolved in 100 mL distilled water under a stirring state for 1 h at room temperature. Next, the resultant solution was adjusted to pH = 8~9 to form a white precipitate by dropwise addition of ammonium hydroxide solution (25 wt%). The resulting precipitate was filtered, completely rinsed with distilled water and dried at 120 °C for around 5 h. Similarly, other precursors except for NaAlO_2 were also used to prepare spinel catalysts. According to reference [22], NaAlO_2 and $\text{Mg}(\text{NO}_3)_2$ were used to synthesize spinel. Prior to use, the catalyst was calcined at demanded temperature in air for 6 h.

2.3. Catalyst characterization

Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-K α radiation. The FTIR spectra of the catalysts were recorded in the range of 500~4000 cm^{-1} on a Nicolet 6700 spectrometer. The morphologic features of the catalysts were determined by scanning electron microscope (Philips XL30 ESEM FEG). The specific surface areas of catalysts were 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 Brunauer-Emmett-Teller (BET) method. Pore size of catalysts was calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model. TG analysis was used with Netzsch STA449 F3 analyser. Surface acid and base properties of the samples were estimated by NH_3 -TPD and CO_2 -TPD, respectively, on a Quantachrome Instrument. The sample (ca. 50~60 mg) was purged with dry Ar (50 mL/min, purity > 99.999vt%) at 500 °C for 1.0 h, followed by reducing the furnace temperature to 80 °C, and switching to a flow of 8v_t% NH_3 /Ar or 10 v_t% CO_2 /Ar for 1 h to execute NH_3 or CO_2 adsorption. Then, the samples adsorbed NH_3 or CO_2 were desorbed in the range of 80~700 °C at a rate of 10 C/min.

2.4. Catalyst evaluation

The synthesis of acetaldehyde from lactic acid over the catalysts was carried out in a fixed-bed quartz reactor with a 4 mm inner diameter operated at atmospheric pressure. The catalyst (ca. 370 mg, 20~40 meshes) was placed in the middle of the reactor and quartz wool was placed in both ends. Firstly, the catalyst was pretreated at the required reaction temperature (ca. 380 °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) was 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 [47,58,59]. The liquid products were condensed using ice-water bath and analysed off-line using a SP-6890 gas chromatograph with a FFAP capillary column connected to a FID. Quantitative analysis of the products was carried out by the internal standard method using *n*-butanol as the internal standard material. GC-MS analyses of the samples were performed using Agilent 5973 N Mass Selective Detector attachment. The reaction tail gas was analysed 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 were calculated according to Eqs. 2 and 3.

$$t_c = \frac{3600 \times 273.15 \times V_{\text{cat}}}{22,400 \times (n_{\text{LA}} + n_{\text{H}_2\text{O}} + n_{\text{C}}) \times T} \quad (1)$$

t_c : contact time (s); V_{cat} : catalyst volume (mL); n_{LA} : the moles of lactic acid passed per hour; $n_{\text{H}_2\text{O}}$: 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).

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

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

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.

3. Results and discussion

3.1. Characterization

3.1.1. XRD and FT-IR

Fig. 1 presented XRD patterns of magnesium aluminate spinel catalysts prepared with different precursors at 1000 °C of calcination temperature. It is evident that all the prepared samples except for sample *f* show a single phase, well matched with the standard spinel (PDF#21-1152). These samples exhibit strong characteristic diffraction peaks at 19.2°, 31.4°, 37.0°, 44.9°, 59.4° and 65.5°, which can be indexed to (111), (220), (311), (400), (511), and (440) diffractions, respectively [5,7]. Compared to other samples (*a~e*), higher intensities of all diffraction peaks indexed to spinel (PDF#21-1152) for sample

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