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One-step aldol condensation of ethyl acetate with formaldehyde over Ce and P modified cesium supported alumina catalyst

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ABSTRACT

Ethyl acrylate (EA) is synthesized by ethyl acetate (EtOAc) with formaldehyde (FA) through aldol condensation with fixed-bed reactor, and a series of Ce–P–Cs/γ-Al₂O₃ catalyst was developed. The catalysts were characterized with XRD, XPS, SEM-EDS, NH₃- and CO₂-TPD, BET, and pyridine FTIR. The influence of acidity and basicity on activity was discussed. Catalytic performances were further improved by the addition of small amounts of Ce. Key reaction parameters, such as amount of metal loading, space velocity and reaction temperature, were also optimized. The optimum condition demonstrated a maximum EA yield of 31.38% and 60.03% selectivity toward EA.

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Introduction

Ethyl acrylate (EA) or acrylic acid ethyl ester is a derivative of acrylic acid. EA is widely used in the production of homo- and copolymers which is used as the raw material in the manufacturing acrylic resins, as further downstream application acrylic resins are used in formulation for paint, industrial finishing and coatings, textile, latex products, and medical items [1–3]. Due to significant market value since 2014–2019 with compound annual growth rate (CAGR) of 4.6% in Asia-Pacific region, the demand for EA has tremendously increased the market value about \$264.5 million in 2014 and presumed to reach \$364.4 million by 2019 [4].

EA products can be obtained through different processes. Propane and propylene oxidation are basic processes through which acrylic acid (AA) and its derivatives are produced [5–7]. Another synthetic route for producing these chemicals is the well-known “Reppe” process. Reppe and coworkers developed a unique method for the direct synthesis of EA and its derivatives by using acetylene and carbon monoxide [8–10]. The most common process for EA production is the direct esterification between AA and ethanol (EtOH), this process is often catalyzed by homogeneous acid catalysts such as sulfuric acid, phosphoric acid [11–13].

Meanwhile, EA production is undoubtedly important. However, previous synthesis processes required more than two steps and the raw materials used for the reaction are fairly expensive. Hence, the development of alternative routes for EA production is urgent and necessary. Aldol condensation is an interesting route for synthesizing EA. The key to realizing this technique is the presence of a highly active catalyst. Two types catalysts have been proposed for aldol condensation: basic catalysts, which often include the oxides or hydroxides of alkali or alkaline earth metals, such as cesium (Cs), sodium (Na), or potassium (K) supported on silica (SiO₂), alumina (Al₂O₃), zirconia (ZrO₂), titania (TiO₂), magnesia (MgO), and acidic catalysts, which consist mainly of oxides of metals such as vanadium (V) oxide (V₂O₅), phosphorus (V) oxide (P₂O₅), and niobium (V) oxide (Nb₂O₅). Basic catalysts allow more extensive conversion as well as relatively low selectivity of the main products than acidic catalysts, and these characteristic are highly disadvantageous. However, both basic and acidic catalysts are highly active during aldol condensation [14–30].

Acid–base bifunctional catalysts are expected to provide important assistance in various industrial applications. Typical acid–base bifunctional catalysts are both weakly acidic and weakly basic. Acid–base pairs are known to simultaneously and efficiently activate molecules via dual coordination to promote reaction. Tanabe and Hölderich [29] surveyed solid acid–base bifunctional catalysts and reported their development and application in industrial processes. In fact, these catalysts are

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presumed to be applicable in at least 14 dehydration and condensation reactions.

Not only acid–base properties, stability of catalyst is also important. Typically, catalyst deactivation occurred by carbon deposition. Ceria-based materials have been widely used as promoter and catalyst support in various applications such as CO oxidation, water–gas shift (WGS) and aldol condensation because of its high lattice oxygen mobility, high oxygen storage capacity, and easily reducible [31]. Furthermore, cerium exhibited acid property. Kalita et al. [32] reported Ce-enhanced activity of mesoporous Ce–Al–MCM–41 catalyst in the alkylation reaction which increasing Ce content and the brønsted acidity increased.

Many attempts to synthesize AA and its derivatives by aldol condensation over solid acid and solid base catalysts have been reported. Vitcha and Sim [14] used alkaline metals such as Na, K, Ca, Cs, and Rb over silica as a catalyst for aldol condensation of acetic acid (AcOH) with formaldehyde (FA). Nebesnyi et al. [15] used B_2O_3 – P_2O_5 – WO_3 /SiO₂, whereas Yang et al. [16] used V–P/SiO₂ as a catalyst for the same reaction. Aldol condensation of propionic acid (PA), methyl propionate (MP) and methyl acetate (MeOAc) with FA to produce methacrylic acid (MAA), methyl methacrylate (MMA) and methyl acrylate (MA) were also studied. Tai and Davis [22] discovered that aldol condensation of PA with FA through the use of bifunctional catalysts such as Cs impregnated alumina, exhibited modest catalytic activity and high selectivity. Aldol condensation was thus reported to be facilitated by a combination of Brønsted acid and base sites on the catalyst surface. Several papers published the reaction between PA, MP or MeOAc and FA [17–23,25–28]. Reports on the reaction between EtOAc and FA which use bifunctional catalyst are unavailable. This paper investigated a one-step aldol condensation, which involved a series of Ce–P–Cs/ γ -Al₂O₃ as a bifunctional catalyst. A highly effective catalyst was prepared, and the reaction was performed under different loading amounts of Ce, P and Cs over γ -Al₂O₃ catalysts, space velocities, and reaction temperatures.

Experiment

Catalysts preparation

EtAc ($\geq 99.5\%$), EtOH ($\geq 99.7\%$), 1,3,5-trioxane ($\geq 99.0\%$), cesium carbonate ($\geq 98.0\%$), diammonium hydrogen phosphate ($\geq 99.0\%$), and ammonium cerium(IV) nitrate ($\geq 99.0\%$) were utilized in this work. γ -Alumina spheres were obtained from a commercial company.

All of the catalysts were prepared through incipient wetness impregnation method. First, γ -Al₂O₃ was ground and sieved to obtain particle sizes of 20–40 mesh. The supporter was dried in an oven at 80 °C for 6 h. To obtain a Cs-impregnated alumina (Cs/ γ -Al₂O₃), cesium carbonate was dissolved in distilled water, dropped into the supporter, incubated at room temperature for 16 h, and then dried in oven at 80 °C for 6 h. P–Cs/ γ -Al₂O₃ was prepared by adding diammonium hydrogen phosphate solution (P solution) into dried Cs/ γ -Al₂O₃, while maintaining the solution at room temperature and then by drying. Ce–P–Cs/ γ -Al₂O₃ was prepared in a similar method. The resultant product was calcined at 550 °C in a stream of air for 8 h. The loading amounts of Cs, P, and Ce were reported as nominal weight percentages.

Catalyst characterization

The XRD patterns of the catalysts were obtained with an X'Pert PRO MPD diffractometer (PAN analytical Co., Ltd.) operated at an accelerating voltage of 45 kV and an emission of 200 mA with Cu K α radiation ($\lambda = 0.15418$ nm). Angle (2θ) was measured in steps of 10° min⁻¹ between 5–90°.

The X-ray photoelectron microscopy (XPS) was performed with 300 W Al K α radiation by using ESCA Lab220i-XL electron spectrometer (VG Scientific).

Scanning electron microscopy (SEM) images and Energy dispersive spectroscopy (EDS) mapping were performed with a Hitachi SUB8020 scanning electron microscope with an operating voltage of 20 kV. Catalysts were directly placed on the stubs by using double faced conductive tape.

NH₃–CO₂ adsorption was measured with an Autochem II 2920 apparatus Micrometrics. For acidity measurements, the samples were placed in a quartz tube and pretreated with a helium flow at 120 °C for 30 min. The temperature was then reduced to 50 °C, and a mixture of 10% NH₃ in helium was passed through the sample at 50 °C for 90 min. The sample was purged with helium at 50 °C for 30 min until the baseline had stabilized. The NH₃ desorption rate was subsequently monitored using a thermal conductivity detector (TCD) at heating rate of 10 °C min⁻¹ up to 700 °C under helium flow. During acidity measurements, basicity was also measured using 10% CO₂ in helium.

The Brunauer–Emmett–Teller (BET) specific surface area, pore mean diameters and pore volumes were derived from N₂ adsorption isotherms at liquid N₂ temperature using a Micromeritics ASAP 2020 apparatus. Prior to measurement, the samples were degassed at 350 °C for 12 h.

Pyridine FTIR was recorded on Bruker Equinox 55 spectrometer equipped with a cell in situ. The samples were pressed into a self-supporting plate (20 mg, 13 mm diameter), and placed in an IR cell. Then, the sample was pretreated under vacuum at 350 °C for 30 min. After the IR cell was cooled at room temperature, pyridine vapor was passed through the cell, and adsorbed for 5 min. The sample was desorbed for 30 min at room temperature, driving the condition to higher vacuum. Then, the cell was scanned at 150 °C for 30 min.

Thermogravimetric analysis (TG-DTA) of the catalyst was performed on TA-60WS/DTG-60H analyzer (Shimadzu) under air flow 200 mL min⁻¹ from room temperature up to 900 °C with heating rate of 10 °C min⁻¹.

The morphology of the catalysts was observed with a JEOL (JEM-2100F) transmission electron microscopy (TEM) operated at 200 kV. The samples were ultrasonically dispersed in absolute ethanol, and small droplets of the suspension were dropped on copper grids coated with a holey carbon film. After evaporation of the solvent, small amounts of catalyst powder remained on the microscope grids.

Reaction procedure

Aldol condensation was carried out in a fixed-bed reactor operated at atmospheric pressure. The reactor was consisted of a stainless steel tube (i.d. \varnothing 2 cm, 50 cm long) mounted vertically to a furnace. The catalyst (6 mL) 4.656 g was placed in the middle of the reactor. 1,3,5-Trioxane was used as the source of FA, and was dissolved in EtOAc with EtOH. The mixed solution of EtOAc, FA and EtOH was injected through a syringe pump from the top of the reactor at a feed flow rate of 0.1 mL min⁻¹. The molar ratio of EtOAc:FA:EtOH was 5:1:1. The reaction occurred at temperatures ranging from 300 °C to 400 °C. Samples were collected and analyzed off-line with GC (Shimadzu BID-2010 Plus) and Rtx[®]-Wax (30 m \times 0.25 mm \times 0.25 μ m) capillary column. Catalyst activity was measured by testing the conversion of EtOAc, the selectivity and yield of EA and acetic acid as a by-product which calculated by equations below.

$$\% \text{ Conversion of EtOAc} = [\text{EtOAc}_{\text{in,mol}} - \text{EtOAc}_{\text{out,mol}}] / \text{EtOAc}_{\text{in,mol}}$$

$$\% \text{ Selectivity of EA} = [\text{Moles of EA} / \text{Total moles of products}] \times 100$$

$$\% \text{ Yield of EA} = \text{Conversion of EtOAc} \times \text{Selectivity of EA}$$

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