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Sodium nitrate modified SBA-15 and fumed silica for efficient production of acrylic acid and 2,3-pentanedione from lactic acid

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ABSTRACT

The catalytic conversion of lactic acid to acrylic acid and 2,3-pentanedione over sodium nitrate-supported mesoporous SBA-15 and fumed silica was studied. The yields of acrylic acid, 2,3-pentanedione, and acetaldehyde are 44.8%, 25.1%, and 13.3%, respectively, over the 23%$NaNO_3$/SBA-15 catalyst. The performance of the catalysts is strongly affected by $NaNO_3$ loading, catalyst texture and porosity, and product diffusion efficiency. A proper control of $NaNO_3$ loading can result in modification catalyst structure for improvement of 2,3-pentanedione selectivity. Under certain reaction conditions, the surface $NaNO_3$ species can readily transform to sodium lactate that functions as active component to catalyze the target reactions.

1. Introduction

Acrylic acid (AA) is a versatile compound widely used in the manufacture of adhesive, paint-additive, and textile-treating agent. The compound is currently produced through a two-step process of partial oxidation of propylene. Propylene, however, is generated in petrochemical processes and is not renewable. With the high consumption of petroleum and the rising cost of propylene, it is desirable to find an alternative way that is environment-friendly for AA production. For many years lactic acid (LA) has been produced through biomass fermentation [1–3]. It is highly demanded in chemical industry, and is produced in large scale at reasonable cost. It is envisaged that LA will emerge as a major biomass-based feedstock in the near future [4].

LA is reactive and can be converted to value-added chemicals through reaction pathways such as those depicted in Fig. 1. Among them, the dehydration and condensation of LA to AA and 2,3-pentanedione, respectively, have attracted much attention. In 1958, Holmen [5] patented the use of a mixture of $CaSO_4$ and $NaSO_4$ to catalyze the dehydration of LA. Three decades later, Paparizos et al. [6] reported AA yield of 43% over ammonia-treated aluminum phosphate, and Sawicki [7] claimed AA yield >50% over Na_2HPO_4 (with $NaHCO_3$ presence) that was supported on silica-alumina. It is noted that certain important aspects are not clearly elaborated in the patent documents. Under the severe conditions of supercritical water, Mok et al. [8] and Lira and McCrackin [9] studied LA dehydration and reported AA yields of ca. 50%. Recently, Ott et al. also performed dehydration reactions in the near-critical as well as supercritical water, and reported medium AA yield [10,11]. It is known that AA yields are closely related to operating parameters such as gas hourly space velocity and LA concentration in feed. It is hence difficult to compare the performance of the reported catalysts. In other words, a higher AA yield may not necessarily imply better catalyst efficiency.

Over phosphates that were loaded on silica-alumina, Gunter et al. [4] observed that the major reaction was LA condensation to 2,3-pentanedione and LA conversion was low. They also studied the conversion of LA over various sodium salts and support materials, and concluded that pure silica of low surface area was the best for suppressing the formation of acetaldehyde and propanoic acid [12]. Spectroscopic investigations [13–15] on the phosphate- and nitrate-containing catalysts revealed that through proton transfer, the supported phosphate and nitrate could react with LA to generate corresponding lactate species, and the generated lactates might function as active species for LA conversion to 2,3-pentanedione and AA. Over $NaNO_3$-containing catalysts, Tam et al. [16,17] systematically studied the influences of operating parameters and observed AA yield of 26.4% under

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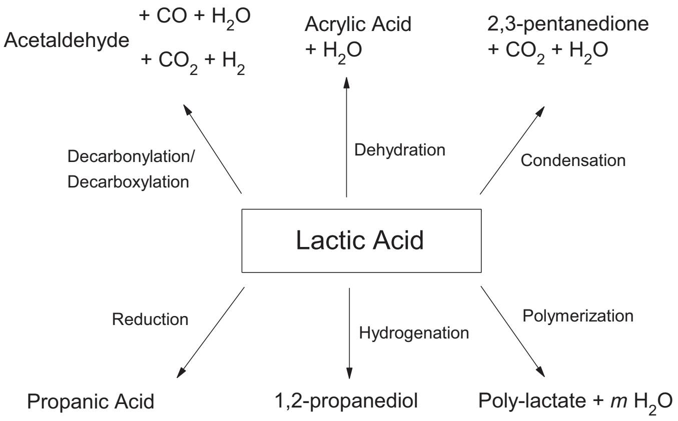

Fig. 1. Possible reaction pathways for LA conversion.

optimized condition. It was also pointed out that among the sodium salts studied; sodium nitrate has the advantages of being low-cost and environment-friendly.

In the present work, we selected mesoporous SBA-15 and non-microporous fumed silica (denoted as FS hereinafter) as support materials, and sodium nitrate as active component. Through the tuning of $NaNO_3$ content, reaction temperature, and LA concentration in solution, we developed an effective catalytic system for the simultaneous generation of AA and 2,3-pentanedione from LA. In the FTIR study of the formation of sodium lactate as a function of time on stream, new information concerning the transformation of sodium nitrate and in situ generation of the active lactate component has been derived.

2. Experimental

2.1. Materials

The LA (analytic grade) was obtained from Sinopahrm Chemical Reagent Co. and deionized water was used for its dilution from 85% to a desired concentration. The FS with a surface area of 204 m^2/g was purchased from Sigma–Aldrich. Triblock copolymer (P123), tetraethyl orthosilicate (TEOS), muriatic acid, $NaNO_3$, and hydroquinone were all purchased from Aldrich. Hydroquinone was added (in certain amount) to LA solution as polymerization inhibitor.

2.2. Catalyst preparation

The SBA-15 was synthesized according to the method described by Zhang et al. [18] and Guo et al. [19]. Briefly, a homogeneous gel was prepared by mixing 3.0 g of P123, 90 g of muriatic acid (2 mol/l), and 22.5 g of water under stirring for 4 h, and 6.78 g of TEOS was added to the gel and the mixture was subject to aging at room temperature (RT) for 24 h and hydrothermal treatment at 100 °C for 48 h. The as-generated solid product was harvested by filtration, washed with deionized water and ethanol, dried at RT, and calcined in a muffle oven at 550 °C for 4.5 h (heating rate = 1 °C/min).

The wet-impregnation approach was adopted for the generation of $NaNO_3$/SBA-15 and $NaNO_3$/FS catalysts. Depending on $NaNO_3$ loading, certain amount of SBA-15 or FS was added into a $NaNO_3$ solution (0.1 mol/l) under stirring. The resulting mixture was heated up to 40 °C, and kept at this temperature for 4 h. The resulting slurry was subject to evaporation at 60 °C (in a rotary evaporator), and subsequently dried at 100 °C (in air) in an oven. Hereinafter, a catalyst of "*x* wt%" loading is denoted as *x*% $NaNO_3$/SBA-15 or *x*% $NaNO_3$/FS.

2.3. Catalyst evaluation

The evaluation of catalyst activity was carried out in a down-flow fix-bed reactor (8 mm in inner diameter and 500 mm in length). The catalyst (0.30–0.35 g) was charged into the reactor, and quartz chips were loaded on top of the catalyst bed to achieve adequate preheating of the incoming LA-containing feed. Before reaction, the reactor was heated (at a rate of 10 °C/min) with pure N_2 (50 ml/min) passing through it to a designed temperature and kept at this temperature for 3 h. Then LA was introduced (by a syringe pump) into the reactor at a liquid flow rate of 5 ml/h (corresponding LHSV = 6 h^{-1}). The product was collected at a cold trap for analysis.

2.4. Product analysis

The collected product was analyzed by gas chromatography using HP-FFAP capillary column and FID, and 100 μl of valeric acid was added to 5 ml of product as internal standard. The main components in the liquid phase were found to be acetaldehyde, 2,3-pentanedione, propanoic acid, AA, and LA. Minor products including ethanol, acetic acid and some unidentified compounds are denoted as "other" products. The main gas products are CO and CO_2, which can be quantified based on the yields of acetaldehyde and 2,3-pentanedione.

2.5. Catalyst characterization

The powder X-ray diffraction measurement was conducted on a Shimadzu XRD-6000 diffractometer operated at 40 kV and 40 mA with Cu-K_a radiation. The specific surface area and pore volume of the catalysts were measured through nitrogen adsorption at 77 K over a Micrometrics ASAP 2020 instrument. Prior to adsorption, the samples were kept under vacuum at 350 °C for 8 h. Ammonia temperature-programmed desorption (NH_3-TPD) was carried out to measure surface acidity of catalysts. Typically, 0.1 g of catalyst was heated in flowing Ar (30 ml/min) at 400 °C for 1 h, and then cooled to 100 °C in the same Ar flow. Ammonia was subsequently introduced, and after NH_3 adsorption the sample was purged with He (30 ml/min). Finally, NH_3-TPD was carried out in He from 100 to 400 °C at a heating rate of 10 °C/min. The signal was recorded by a thermo-conductive detector.

The IR spectra of fresh and used catalysts were recorded on a Bruker VERTEX 70 spectrometer (in the range of 1000–4000 cm^{-1}) for the checking of transformation of surface nitrate during reaction. TG/DTA measurement was conducted on a NETZSCH STA-449C integrated thermo-analysis instrument with the sample heated in air at a rate of 10 °C/min from RT to 700 °C.

3. Results and discussion

3.1. Characterization

The XRD patterns of the $NaNO_3$/SBA-15 samples indicated that the ordered mesoporous structure of SBA-15 is basically retained (Fig. 2a and b). With the increase of $NaNO_3$ loading on SBA-15, there is a gradual decline of peak intensity and a shift of peak position within the small-angle range ($2\theta = 0.7–5°$). The results suggest that to a certain degree the presence of $NaNO_3$ causes a decline in SBA-15 structural regularity (such as mesoporous porosity). In the case of FS, with the rise of $NaNO_3$ loading one observes monotonous increase of $NaNO_3$ peak intensity (Fig. 2c). Such monotonous rise of $NaNO_3$ peak intensity is not observed over the $NaNO_3$/SBA-15 catalysts (Fig. 2b), reflecting the difference in texture/porosity of the two kinds of catalysts. The results of NH_3-TPD investigation showed no obvious desorption over the $NaNO_3$/