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Article

One-step aldol condensation reaction of dimethoxymethane and methyl acetate over supported Cs/ZSM-35 zeolite catalysts

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ABSTRACT

This study was performed for the development of a green and promising approach for the synthesis of methyl acrylate and acrylic acid by a one-step aldol condensation reaction of dimethoxymethane and methyl acetate over cesium oxide-supported on ZSM-35 zeolite catalysts; the effect of base sites as well as acid sites on the aldol condensation reaction was studied in detail. It was found that base sites were harmful for aldol condensation due to their failure in catalyzing the decomposition of dimethoxymethane precursor into formaldehyde, whereas the acid site was indispensable for the reaction to proceed. This reaction cannot take place without an acid site. Although acid sites in H-form of the zeolite (HZSM-35) are indispensable for the aldol condensation reaction, not all of them tend to favor this reaction. A strong acid catalyzes methanol-to-olefin-like reactions resulting in hydrocarbon byproducts, which are finally transferred to hard coke. Medium strong acids and weak acids are great candidates for the target aldol condensation reaction with high activity and selectivity. A γ-Al_2O_3 sample with abundant weak-strength Lewis acid sites, together with a few medium-strong-strength acid sites, performs well with a high activity and considerable stability during the synthesis of methyl acrylate and acrylic acid.

1. Introduction

Acrylic acid (AA) and methyl acrylate (MA), widely used for paintings, coatings, carbon fibers, and adhesives, are presently produced by the two-step oxidation of propylene [1–5]. In this process, propylene is oxidized with oxygen/air to produce acrolein followed by oxidation of acrolein to AA. After the esterification of AA with methanol, AA is converted into MA. However, this two-step process is accompanied by the over-oxidation of propylene, resulting in a low selectivity of AA, and further poses a risk of explosion due to the direct mixing of hydrocarbons with oxygen/air, which limits the widespread application of this route. Therefore, it is highly necessary to develop a novel green route for MA and AA synthesis.

The synthesis of MA and AA through the one-step aldol condensation reaction of formaldehyde with methyl acetate (MAc) has attracted substantial interest and concern from both academic and industrial communities in the past few decades because of its simplified reaction route and common feedstocks, which can be readily derived from natural gas, coal, and

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biomass [6,7]. This reaction has been reported to be catalyzed by acids, bases, or base-acid bifunctional catalysts, among which acid-base bifunctional catalysts attract most attention owing to their good performance in aldol condensation reactions as a result of cooperation between their acid and base active sites. For example, it was reported that the yield of methyl methacrylate over supported cesium oxide catalysts was not more than 23.0% during the aldol condensation reaction of methyl propionate and formaldehyde [8,9], but the yield was doubled over cesium catalysts doped with other metals with acid-base bifunctional properties [10]. In addition, V–P oxide catalysts attract much academic attention owing to their similar acid-base bifunctional properties. Spivey et al. [11] evaluated at least 80 catalytic materials and found V oxides supported on amorphous silica to be the most effective. Ai [12–17] conducted the aldol condensation reaction of propionic acid with formaldehyde over V–P–Si samples and obtained a yield of 70% at the optimum experimental conditions. Gogate et al. [18] studied the vapor phase aldol condensation reaction of formaldehyde with propionate derivatives over a series of V–P–Si catalysts of varying atomic ratios and obtained a maximum methacrylic acid yield of 56%. V–P–Si catalysts also perform well in the aldol condensation reaction of formaldehyde with other carbonyl compounds, such as acetone or acetaldehyde [19–21].

The effect of the acid-base bifunctional property of V–P–Si ternary oxide catalysts was studied in the case of the aldol condensation of acetic acid or methyl acetate with formaldehyde to prepare MA and AA. Hu et al. [22] prepared V–P–Si catalysts with high acid and alkali quantities by the incipient wetness impregnation method and found that the activities of these catalysts for the conversion of formaldehyde increased with an increase in the alkali quantity, while the selectivity for acrylic acid increased with an increase in the acid quantity. This means that the acid-base properties of these catalysts play a significant role in enhancing both precursor conversion and product selectivity. Yang et al. [23] found that weak base sites were essential for aldol condensation, while weak acid sites were responsible for improvement in the selectivity of acrylic acid over a series of V–P–Si catalysts. Feng et al. [24] studied the correlation between the catalyst structure and constitution of a V–P catalyst and its performance in the aldol condensation reaction of acetic acid or methyl acetate and formaldehyde and found that catalysts containing medium-strong acid sites of high density performed much better. In our previous work on the aldol condensation reaction of formaldehyde with methyl acetate over a pure acidic H-form of a zeolite to produce MA and AA, we reported an optimum yield as high as 61.1% [25]. It seems that base sites as well as acid sites are greatly helpful in catalyzing aldol condensation reactions.

Herein, we prepared a series of zeolites supported by varying weight percentages of cesium oxide by an incipient wetness impregnation method in order to study the effect of base sites or acid sites on the performance of the aldol condensation reaction. Dimethoxymethane (DMM) was used as the source of formaldehyde. The textural and acid-base properties of these samples were characterized in detail and their relationship with the performance of the aldol condensation reaction was illustrated.

2. Experimental

2.1. Catalyst preparation

Zeolites (ZSM-35) and γ–Al_2O_3 were purchased from the Shanghai Zhuoyue Chemical Limited Company, China. The zeolite sample was converted into a H-form of HZSM-35 before use by conducting ion exchange thrice at 80 °C for 6 h in 1 mol/L NH_4NO_3, followed by washing with deionized water, drying at 100 °C overnight, and calcination at 550 °C for 4 h.

To synthesize the zeolite-supported alkaline metal cesium oxide catalysts, the HZSM-35 zeolite precursor was impregnated with an aqueous solution containing varying amounts of Cs_2CO_3. The mixture was heated with stirring at 50 °C for at least 5 h until a paste-like material is formed and then dried in an oven. The dried sample was calcined in flowing air at 500 °C for 4 h. The sample was denoted as Z–Cs–X, where Z denotes zeolite and X refers to the weight percentage of the alkaline metal. Before use, the sample powder was pressed and sieved to obtain particles in the size range of 20–40 mesh. We also prepared silica-supported alkaline metal oxide samples using a similar method.

2.2. Characterization

The crystallinities of the samples were characterized by a PANalytical X'Pert PRO X-ray diffraction (XRD) instrument with Cu K_α radiation (λ = 1.51059 Å) at 40 kV and 40 mA.

The total surface area was calculated according to the Brunauer-Emmett-Teller (BET) equation. The micropore volumes and micropore surface areas were evaluated using the *t*-plot method. The mesopore volumes were calculated using the Barrett-Joyner-Halenda (BJH) method.

The bulk acidity of the zeolite was determined by the temperature-programmed desorption of ammonia (NH_3-TPD) on a Micromeritics AutoChem 2920 instrument. The sample (0.2 g) was loaded in a U-shaped microreactor and preheated at 550 °C for 0.5 h in a helium atmosphere. After cooling to 100 °C, the sample was saturated with ammonia, followed by purging with helium to remove physically adsorbed ammonia molecules. Ammonia desorption was conducted in a flowing helium atmosphere (30 mL/min) by heating from 100 to 650 °C at a rate of 10 °C/min; desorption was analyzed using a thermal conductivity detector (TCD).

Fourier transform infrared (FT-IR) spectroscopy was conducted at a spectral resolution of 4 cm^{-1} on a Bruker Tensor 27 FT-IR spectrophotometer equipped with a mercury-cadmium-telluride (MCT) detector, which was sensitive to –OH group vibrations. The sample was pressed into a self-supporting disk with a diameter of 13 mm. The disk was then put in a quartz cell connected to a vacuum system, sealed with CaF_2 windows, and then heated up to 450 °C for at least 4 h to remove any retained water before collecting the spectra. Pyridine adsorption was analyzed by exposing the preheated