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Vapor-phase Beckmann rearrangement of cyclohexanone oxime over $B_2O_3/TiO_2–ZrO_2$: the effect of catalyst calcination temperature and solvent

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Abstract

The effect of calcination temperature (500–700 °C) on the performance of $B_2O_3/TiO_2–ZrO_2$ catalyst for vapor-phase Beckmann rearrangement of cyclohexanone oxime to caprolactam was investigated. Catalysts were characterized by adsorption of nitrogen, X-ray diffraction and ammonia temperature-programmed desorption. The results indicated that the percent of acid sites of medium strength within the total acid sites and the pore size both increased with calcination temperature. Such increases led to increases of the oxime conversion and caprolactam selectivity. However, a large amount of crystalline B_2O_3 appeared after calcination at 700 °C and caused the decrease of the total amount of acid sites, which resulted in remarkable decrease in the activity of the catalyst. Another part of this work focused on the effect of solvent on the catalytic performance of $B_2O_3/TiO_2–ZrO_2$. Solvents with various polarities were investigated for the reaction. It was found that acetonitrile, which has the highest polarity for solvents examined here, was the most effective for the formation of caprolactam. The solvent with high polarity increases the desorption rate of produced caprolactam from catalyst surface, resulting in a high selectivity to caprolactam and low catalyst deactivation rate. FT-IR measurements confirmed the efficient desorption of caprolactam induced by the attack of the acetonitrile molecule.

Keywords: Beckmann rearrangement; Cyclohexanone oxime; Caprolactam; $TiO_2–ZrO_2$ mixed oxide; Boria catalyst; Calcination temperature; Acetonitrile

1. Introduction

Caprolactam is an industrially important raw material for the production of nylon-6 fibers and resins. The most important route to produce caprolactam is the Beckmann rearrangement of cyclohexanone oxime catalyzed by fuming sulfuric acid in the liquid phase. Although the process is highly selective, it has a number of significant shortcomings, such as the production of large amounts of low value ammonium sulfate, the corrosion of equipment, and environmental pollution caused by the use of sulfuric acid. In order to overcome the above-mentioned problems, researchers have conducted extensive studies on the Beckmann rearrangement reaction without sulfuric acid, especially in the vapor-phase over solid acid catalysts. Boria catalysts supported on various carriers have been studied most extensively [1–10]. As the support of boria, the single metal oxides have mainly been studied, such as alumina [1–3], silica [4], thoria [5], titania [6] or zirconia [7–9]. Recently, we reported that the performance of boria catalyst supported on $TiO_2–ZrO_2$ mixed oxide ($B_2O_3/TiO_2–ZrO_2$) in the vapor-phase Beckmann rearrangement reaction was much better than those of other boria catalysts supported on TiO_2, ZrO_2 and on other binary oxides based on SiO_2, Al_2O_3, TiO_2 and ZrO_2 [11–13].

It is well established in the literature that the performance of supported boria catalyst is strongly dependent on the calcination temperature of the catalyst [8,9,14–17]. For

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example, Curtin et al. [14] found that the B_2O_3/Al_2O_3 catalyst prepared by calcining at 500 °C showed better caprolactam yield than that calcined at 350 °C. Recently, Xu et al. [8] reported that, for the B_2O_3/ZrO_2 catalyst prepared by pre-calcining $Zr(OH)_4$ at 300 °C, followed by impregnating with boric acid and calcining, the increase in calcination temperature from 350 to 600 °C resulted in dramatically improved selectivity and yield of caprolactam; the caprolactam selectivity increased from 70–80% to values greater than 95%, and the caprolactam yield increased from ca. 70 to 92%. Therefore, it is worthwhile to study the effect of calcination temperature on the catalytic performance of $B_2O_3/TiO_2–ZrO_2$ catalyst in the vapor-phase Beckmann rearrangement of cyclohexanone oxime.

Moreover, much attention has recently been focused on the effect of solvent on the Beckmann rearrangement reaction over solid acid catalysts. Results showed that the caprolactam selectivity and catalyst lifetime could be improved greatly by using suitable solvent. For example, Kob and Drago [18] observed that the solvent methanol increased the caprolactam selectivity of WO_3/SiO_2 catalyst as compared with methylene chloride and benzene. On the other hand, Komatsu et al. [19] reported that ethanol and methanol are the most effective solvents for the vapor-phase Beckmann rearrangement of cyclohexanone oxime on silicate-1, while alcohols with higher carbon numbers such as 1-hexanol lowered the caprolactam yield due to their hydrophobic nature. By contrast, Tatsumi and co-workers [20–23] found that 1-hexanol gave the best selectivity to caprolactam among C_1–C_7 1-alcohol solvents over proton exchanged large pore size (12 MR) zeolites. These results indicate that the effect of solvent on the Beckmann rearrangement reaction was strongly dependent on the kind of catalysts. Furthermore, even though a large number of investigations on the effect of solvents have been made, there are few definite explanations of the reason for the improvement of catalytic performance by the specific solvents [19].

In the present paper, the influence of calcination temperature on the performance of $B_2O_3/TiO_2–ZrO_2$ catalyst for vapor-phase Beckmann rearrangement of cyclohexanone oxime was investigated. The physicochemical properties of catalysts calcined at different temperatures were characterized by X-ray diffraction (XRD), adsorption of nitrogen and temperature-programmed desorption of ammonia (NH_3-TPD); results were correlated to catalytic behavior. Besides, the vapor-phase Beckmann rearrangement of cyclohexanone oxime over $B_2O_3/TiO_2–ZrO_2$ catalyst was carried out using a variety of solvents with different polarities in order to further improve its catalytic performance by selecting a suitable solvent. Moreover, the effect of solvent on selectivity and stability of $B_2O_3/TiO_2–ZrO_2$ catalyst was discussed based on the desorption behavior of the adsorbed caprolactam caused by the attack of solvent molecules as observed by FT-IR spectroscopy.

2. Experimental

2.1. Catalyst preparation

The support, $TiO_2–ZrO_2$, with a molar ratio of 1:1 was prepared by a co-precipitation method using aqueous ammonia as a precipitation reagent, as described previously [11–13]. In brief, the equal moles of $TiCl_4$ and $ZrOCl_2\cdot 8H_2O$ (provided by Shanghai Chemical Reagent Corporation, AR grade) were dissolved separately in deionized water. Then the two solutions were mixed at room temperature under vigorous stirring. The mixture was added to an excess amount of aqueous ammonia slowly and this combination was mixed thoroughly by control of the final pH at 9.0 ± 0.2. The precipitate was allowed to stand at room temperature overnight, then filtered off and washed several times with deionized water until free from chloride ions. The solid obtained was dried at 110 °C overnight and then calcined for 6 h in air at 500 °C. Finally, the support was pressed into wafers, crushed and sieved to 40–60 mesh before use for impregnation of B_2O_3. The resulting $TiO_2–ZrO_2$ mixed support had a N_2 BET surface area of $170\ m^2\ g^{-1}$.

The catalysts, $B_2O_3/TiO_2–ZrO_2$, which contained 12 wt.% (nominal) of B_2O_3 were prepared by impregnating the support with an aqueous solution of boric acid (Analytical Grade, Shanghai Chemical Reagent Corporation, PR China) using incipient wetness techniques. The impregnated catalysts were dried at 110 °C overnight and then calcined at various temperatures (from 500 to 700 °C) for 12 h in a closed electrical furnace in open air atmosphere. The rate of heating was maintained at $10\ °C\ min^{-1}$. These catalysts were labeled as B/TZ-*T*, where *T* stands for the calcination temperature in °C.

2.2. Catalyst characterization

The catalysts prepared by calcining at different temperatures were characterized by X-ray diffraction (XRD) and adsorption of nitrogen as well as by temperature-programmed desorption of ammonia (NH_3-TPD).

X-ray diffraction (XRD) patterns were collected with a Rigaku D/MAX-1400 (Japan) instrument, equipped with a graphite monochromator, operated at 40 kV and 40 mA and using nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

The BET surface area and pore size of the $B_2O_3/TiO_2–ZrO_2$ catalysts were measured on a Micromeritics Digisorb 2600 system (USA) under liquid-N_2 temperature using N_2 as the adsorbate. Prior to analysis, all samples were outgassed under vacuum at 450 °C for 3 h to evacuate the physisorbed moisture.

Acidity measurements were performed by temperature-programmed desorption of ammonia (NH_3-TPD) using a conventional flow apparatus equipped with a thermal conductivity detector (TCD). A given amount of the samples, 0.1 g, was pretreated in flowing helium at 500 °C for 1 h. After cooling down to 150 °C, the adsorption