

Vapor-phase Beckmann rearrangement of cyclohexanone oxime over $\text{H}_3\text{PO}_4/\text{ZrO}_2\text{-TiO}_2$

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Received 7 September 2004; received in revised form 8 March 2005; accepted 25 March 2005

Abstract

$\text{ZrO}_2\text{-TiO}_2$ mixed oxides with a Ti and Zr molar ratio of 1/1 were prepared under various conditions by the sol–gel method. Catalysts containing 5–35% H_3PO_4 were prepared using these oxides and the catalytic performance of each material for vapor-phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam was determined. As the H_3PO_4 content in the mixed oxide increased, the specific surface area decreased; XRD results indicated that $\text{ZrO}_2\text{-TiO}_2$ became amorphous after calcinations at 700 °C. The yield of lactam increased with increasing the H_3PO_4 content in the mixed oxide and reached a maximum value for the 15 wt.% H_3PO_4 on the $\text{ZrO}_2\text{-TiO}_2$ (1/1) support. With further increase in H_3PO_4 content, the lactam yield decreased; the lowest value was observed for the 35 wt.% H_3PO_4 on the $\text{ZrO}_2\text{-TiO}_2$ (1/1) support. The acidic properties and the pore characteristics of the catalysts were key factors that affected its performance. The influences of the operating parameters on the performance of $\text{H}_3\text{PO}_4/\text{ZrO}_2\text{-TiO}_2$ (1/1) catalyst were also investigated. The interaction of H_3PO_4 with $\text{ZrO}_2\text{-TiO}_2$ (1/1) support has been investigated by FT-IR, for characterization of the interaction of H_3PO_4 with the support.

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Keywords: Beckmann rearrangement; ϵ -Caprolactam; Cyclohexanone oxime; H_3PO_4 ; TiO_2 ; ZrO_2

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam, which is the precursor to nylon-6 is traditionally being carried out using fuming sulfuric acid as a catalyst. However, this process yields more undesirable ammonium sulfate than the desired lactam. This technique is not environmentally friendly and is considered to be one of the most inefficient chemical processes. Moreover, the use of corrosive sulfuric acid should be avoided for environmental and economic reasons. Chemists have long desired that this process be replaced by one that is based on solid acid catalyst [1,2]. Up to now, there have been mainly two types of solid acid catalysts that have been explored in the literature for the Beckmann rearrangement. One type is based on zeolites or zeolitic materials [2–6]; the other is based on boria supported on oxide supports [7–10].

Recently, Sumitomo Chemical Co., developed a vapor-phase Beckman rearrangement process for the production of ϵ -caprolactam [11]. In this process, cyclohexanone oxime is rearranged into ϵ -caprolactam using a catalyst mainly composed of high-silica MFI zeolite instead of sulfuric acid.

Previous researchers have highlighted the use of single component oxides such as alumina, silica, thoria, titana and zirconia as supports for boria-based catalysts for the Beckmann rearrangement. Recently, Mao and coworkers reported new results for the vapor-phase Beckmann rearrangement of cyclohexanone oxime over B_2O_3 catalysts supported on various binary oxides based on SiO_2 , Al_2O_3 , TiO_2 and ZrO_2 . Among these catalysts, $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$, with the highest selectivity and yield of lactam, was studied as a function of the oxide composition. The yield of lactam increased with increasing zirconia content in the mixed oxide and reached a maximum value for the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ (1/1) catalyst [12].

In the present study, we show that the catalytic performance of $\text{H}_3\text{PO}_4/\text{ZrO}_2\text{-TiO}_2$ (1/1) is superior to boria

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supported on $\text{ZrO}_2\text{-TiO}_2$ (1/1). FT-IR and XRD measurements are performed to characterize the structure and acidity of the catalysts with different H_3PO_4 loads. Responses of catalytic performance to the changes of H_3PO_4 load and to using a template during the preparation of the $\text{ZrO}_2\text{-TiO}_2$ support are reported to clarify the relationships among H_3PO_4 load, surface area of the catalyst, surface acidity and the catalytic performance for the Beckmann rearrangement.

2. Experimental

$\text{ZrO}_2\text{-TiO}_2$ (1/1) was used as the support. This support was prepared by the sol–gel method. Zirconium(IV) isopropoxide (70 wt.% solution in 2-propanol) and titanium(IV) *n*-butoxide (99%) were used as the precursors, and 2,4-pentandione (H-acac) as the complexing agent [13,14]. Appropriate amounts of zirconium propoxide and titanium *n*-butoxide were dissolved in the solvent, *n*-butanol. The solution was heated to 60 °C. The components were thoroughly mixed. Then the solution was cooled down to room temperature, and H-acac as the complexing agent was added. This clear solution was divided in two parts. The first portion was hydrolysed with deionized water (11.0 mol H_2O /mol alkoxide), and the second portion was hydrolyzed with deionized water containing cetyl pyridinium bromide (CPB) surfactant (mol surfactant/mol alkoxide = 0.1). The solutions were left overnight to hydrolyze the alkoxides, yielding transparent gels. The transparent gels were dried at 110 °C to remove water and solvent, and then calcined at 500 °C for 5 h to remove the organics. The supports are denoted as $\text{ZrO}_2\text{-TiO}_2$ (1/1), and $\text{ZrO}_2\text{-TiO}_2$ (1/1)-surf.

A series of catalysts with varying H_3PO_4 contents were prepared by impregnating calculated amounts of H_3PO_4 dissolved in deionized water on $\text{ZrO}_2\text{-TiO}_2$ supports. The impregnated catalysts were dried at 110 °C for 12 h and then calcined in air at 500 °C for 6 h. All the impregnated catalysts were pressed into wafers, crushed and sieved to 20–40 mesh before use.

The Beckmann rearrangement of cyclohexanone oxime was conducted at 280–330 °C under atmospheric pressure in a flow pyrex reactor (i.d. 8 mm) with 0.5 g catalyst. A mixture of the oxime and solvent was passed into the reactor at $\text{WHSV} = 1.2 \text{ h}^{-1}$ in terms of oxime. The oxime was dissolved in the solvent (toluene, ethanol or acetonitrile) (20 wt.%) and was fed into the reactor with an infusion pump (GENIE, Kent Scientific Corporation). Before each run of the reaction, the catalyst was preheated at 450 °C for 2 h in a flow of dry nitrogen (50 ml/min). Usually, the initial 30 min of the reaction was deducted from the reaction time-on-stream (TOS) since material balance during this initial period was poor. After this 30 min of reaction, products from the reactor were collected each hour in an ice/water trap and were analyzed using a GC (Shimadzu model 14A) equipped with a (2 m) packed OV-17 column and an FID detector.

FT-IR spectra of the catalyst were recorded on a Bruker IFS-66 single channel Fourier transform spectrophotometer with the KBr pellet method.

BET surface area and pore size distribution were measured on a Micromeritics Digisorb 2600 system at liquid N_2 temperature using N_2 as adsorbate. Before measurements, the samples were dried in situ at 450 °C for 3 h under vacuum.

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-1400 instrument at 40 kV and 40 mA using Cu $\text{K}\alpha$ radiation over a 2θ range from 5° to 100°.

3. Results and discussion

3.1. Influence of surfactant on the mixed oxide

$\text{ZrO}_2\text{-TiO}_2$ (1/1) and $\text{ZrO}_2\text{-TiO}_2$ (1/1)-surf were each used as the support. These supports were prepared by the sol–gel method, as mentioned in Section 2. The specific surface areas of the isolated mixed oxides are reported in Table 1. The surface area of the mixed oxides prepared in the presence of surfactant is about 10% higher than the other samples, and more interestingly these mixed oxides show higher selectivity and activity in the optimized conditions, as represented in the following sections. Depending on the hydrolysis–condensation rate of titanium or zirconium alkoxides, in the presence or absence of surfactant, the particle agglomeration behavior could be affected and the different textural properties of the mixed oxides are a result of such effects.

The infrared spectra of the $\text{H}_3\text{PO}_4/\text{ZrO}_2\text{-TiO}_2$ catalysts (without surfactant) are not very informative (Fig. 1), but the infrared spectra of the $\text{H}_3\text{PO}_4/\text{ZrO}_2\text{-TiO}_2\text{-surf}$ catalysts are more informative (Fig. 2). They show two broad absorption bands at 1300–1500 and 850–1000 cm^{-1} , and a relatively sharp absorption band at 1040 cm^{-1} . The band at 1300–1500 cm^{-1} shifts toward a higher frequency, and the bands at 850–1000 cm^{-1} and 1040 cm^{-1} grow in proportion with the H_3PO_4 load. The band at 1500 cm^{-1} belongs to the O–H in-plane bending vibration. The absorption bands at 850–

Table 1
BET surface area and pore volume data for catalysts

Sample	BET SA (m^2/g)	BJH pore volume (cm^3/g)	Total pore volume (cm^3/g)
5PZrTi ^a	213	0.0345	0.0592
15PZrTi	201	0.0296	0.0497
25PZrTi	188	0.0199	0.0456
35PZrTi	150	0.0187	0.0366
5PZrTi-surf ^b	246	0.0383	0.0639
15PZrTi-surf	221	0.0266	0.0605
25PZrTi-surf	192	0.0209	0.0425
35PZrTi-surf	165	0.0217	0.0418

^a 5PZrTi represents a sample containing 5% H_3PO_4 without surfactant.

^b 5PZrTi-surf represents a sample containing 5% H_3PO_4 with surfactant.

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