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Active and selective catalyst for liquid phase Beckmann rearrangement of cyclohexanone oxime

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Abstract

The effect of acid treatment on the catalytic performance of ultrastable Y catalysts in the Beckmann rearrangement of cyclohexanone oxime has been investigated under liquid phase conditions. Over the catalysts treated under mild conditions, enhanced activity was observed due to an increase in the amount of Brønsted acid sites, but a considerable amount of extra-framework aluminum (EFAL) with Lewis acidity remained, resulting in a rapid loss of selectivity to ε-caprolactam. Under relatively severe conditions, the extensive removal of EFAL improved the lactam selectivity, although the extraction of framework aluminum resulted in decreased oxime conversion. Pyridine and benzonitrile adsorption studies indicated the presence of at least two different kinds of Lewis acid sites in the catalysts. The relationships between the catalytic performance and Fourier transform infrared spectroscopy suggested that weak Brønsted acid sites are the active centers for the rearrangement reaction, whereas weak Lewis acid sites due to an extra-framework amorphous phase are responsible for the cyclohexanone formation. Thus the catalyst with weak Brønsted acid sites and a small amount of acidic EFAL species is active and selective for the liquid phase Beckmann rearrangement of cyclohexanone oxime.

Keywords: Beckmann rearrangement; Ultrastable Y; Extra-framework aluminum; Benzonitrile

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime is an important step in the production of ε-caprolactam, a valuable starting material for the manufacture of nylon-6. In the current commercial process, oleum is used mainly stoichiometrically. It carries many serious drawbacks, including high ammonium sulfate formation as a byproduct during the neutralization step to liberate the lactam produced. As a promising solution, replacing this environmentally unfriendly process with heterogeneous catalysis over solid acid materials has been investigated over the last decade [1–19].

Due to a high basicity of lactam, the reaction has been carried out under drastic conditions at temperatures of 300–350 °C, to facilitate the desorption of the lactam product from acid sites [1–17]. This consequently accelerates the side reactions giving various basic compounds and coke formation, often resulting in a rapid decay of catalytic activity. Sumitomo Chemical Company uses a fluidized-bed system to continuously remove carbonaceous deposits from the catalyst in the recently commercialized vapor phase process [20]. Alternatively, performing the reaction under relatively mild liquid phase conditions in the presence of a suitable solvent would minimize the byproducts and prolong the service life of catalysts [18,19]. It would also be expected to provide a more energetically and economically favorable route for the production of caprolactam.

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Subjects on the active sites responsible for the formation of ε-caprolactam have been studied extensively [1–19]. Under vapor phase conditions, the weakly acidic hydroxyl groups [5–8] and even the neutral silanols [9] have been suggested to be active and selective, whereas the presence of strong acid sites results in the formation of byproducts [10,11]. In contrast, it has been shown that Brønsted acidity is of importance, whereas silanol sites are involved in cyclohexanone formation at low temperatures [19]. This reflects the superior performance of Brønsted acid sites to weakly acidic hydroxyl groups in the liquid phase rearrangement.

Ultrastable Y (USY) zeolite with the faujasite (FAU) structure, having a three-dimensional network of supercage cavities connected by 12-membered ring windows with a large diameter of 7.4 Å, is commercially prepared by high-temperature steaming of ammonium or proton-form Y zeolite. In addition to the Brønsted and Lewis acidity in the parent material, the formation of a relatively large number of weakly acidic hydroxyl groups and the existence of transient hydroxylated aluminum [21] and various species of extra-framework aluminum (EFAL) (e.g., cationic aluminum ions [22,23] and silica-alumina amorphous phase [24–26]), have been proposed. It is believed that some EFAL species confer Lewis acidity of different strengths [27–30] and that some species have a synergistic effect with Brønsted acid sites, resulting in increased acid strength and catalytic activity [31–33].

Our previous study on the effect of water addition over HUSY catalyst showed that Lewis acid sites are responsible for the formation of cyclohexanone through the hydrolysis of cyclohexanone oxime [34]. A part of these Lewis acid sites is due to EFAL species, which can be leached out by simple acid washing [26,29,31,35]. Moreover, the acidic properties and performance of catalysts can be adjusted by varying the treatment conditions [3,31].

In the present investigation we studied the liquid phase Beckmann rearrangement of cyclohexanone oxime over several samples of USY catalysts prepared by acid treatment. The acidic properties were characterized with Fourier transform infrared (FTIR) spectroscopy. These results were considered in light of catalytic performance, to identify the active sites responsible for the rearrangement and relevant reactions.

2. Experimental

2.1. Catalyst modifications

Commercially available proton-form USY and beta zeolites with the SiO_2/Al_2O_3 ratio of 7 and 25, respectively, were supplied by Tosoh. To dealuminate the parent USY sample (HUSY-7), typically an aqueous solution of HNO_3 or HCl with different concentrations was used. The solid-to-liquid ratio was kept constant at 1:40. As shown in Table 1, reaction temperature and time were also varied to achieve catalysts with a desired Al content. For beta zeolite, it was similarly ion-exchanged using an aqueous solution of NH_4NO_3. The solid products were recovered by filtration, washed many times with distilled water, dried at 120 °C overnight, and calcined at 500 °C for 6 h. The dealuminated samples were designated as DeUSY-X, where X indicates the SiO_2/Al_2O_3 ratios of the product sample, whereas the obtained beta catalyst with the SiO_2/Al_2O_3 ratio of 36 was designated as HBEA-36.

Table 1
Treatment conditions and structural properties of catalysts used in the present study

Catalyst[a]	Solution	Temperature (°C)	Time[b] (h)	Crystal-linity[c] (%)	Unit cell[d], a_0 (Å)
HUSY-7	–	–	–	100	24.37
DeUSY-11	0.1 M HNO_3	80	3	107	24.37
DeUSY-24	0.2 M HNO_3	25	2	89	24.31
DeUSY-33	0.5 M HNO_3	25	2	56	24.18
DeUSY-35	0.1 M HNO_3	80	2*	98	24.33
DeUSY-40	0.5 M HCl	25	2	67	24.25
DeUSY-63	0.15 M HNO_3	80	2*	62	24.22
HBEA-36	0.5 NH_4NO_3	80	2	–	–

[a] Number after hyphens indicates the SiO_2/Al_2O_3 ratio.
[b] Asterisk means that the treatment was repeated.
[c] Relative to XRD pattern of the parent HUSY-7.
[d] Calculated from the diffraction peak corresponding to (533) reflection plane.

2.2. Reaction procedure

Before applied to the reaction, catalysts were activated at 500 °C for 6 h in a muffle furnace and then allowed to cool down inside a desiccator to prevent adsorption of water in the atmosphere. The Beckmann rearrangement was typically carried out in a 50-ml flask at 130 °C under nitrogen atmosphere, using benzonitrile (PhCN) as a solvent. The amount of catalyst used was 0.1 g, and the catalyst:oxime:PhCN composition was 1:1:200 (weight). The reaction progress was followed by timely sampling and subsequent analysis of product distribution with a gas chromatograph equipped with a 30-m capillary column of PEG.

2.3. Characterizations

FTIR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. A 30-mg sample was pressed into a self-supported, 20-mm-diameter wafer. The wafer was set in a quartz infrared (IR) cell that was sealed with CaF_2 windows and connected to a vacuum system. In pyridine and PhCN adsorption experiments, the wafer was evacuated at 500 °C for 1 h, followed by exposure to a desired amount of pyridine and PhCN vapor for 1 h at 100 and 35 °C, respectively. The desorption of pyridine was carried out stepwise at 100 and 150 °C for 1 h at each temperature. The introduction of PhCN vapor