Catalytic dehydrogenation and cracking of industrial dipentene over M/SBA-15 (M = Al, Zn) catalysts

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Abstract

Al- and Zn-containing mesoporous molecular sieves (SBA-15) were prepared by an impregnation method and were used as catalysts for the catalytic dehydrogenation and cracking of industrial dipentene, an important natural feedstock. The catalysts were characterized by X-Ray fluorescence spectroscopy (XRF), X-Ray diffraction (XRD), N_2 adsorption/desorption, transmission electron microscopy (TEM), magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) and Fourier transform infrared spectroscopy (FT-IR) techniques. The characterization results suggest that the active components were introduced without changing the mesostructure of SBA-15. FT-IR revealed that Al/SBA-15 shows weak Brönsted acidity and strong Lewis acidity, while Zn/SBA-15 only possesses moderate Lewis acidity. Dehydrogenation and cracking products, such as toluene, were found in the dipentene conversion over Al/SBA-15, while for Zn/SBA-15, *p*-cymene was the major dehydrogenation product. Along with the strong Brönsted acidity and high cracking activity of HZSM-5, our results suggest that the reaction pathway is determined by the acidic sites. Stability tests showed the deactivation is also related to the acidity. The highest yield of *p*-cymene reaches to 86.7% on Zn/SBA-15 at 723 K.
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1. Introduction

The conversion of terpenes to high value products is of high environmental and commercial interest [1,2]. As the by-product of camphor preparation and pulp-paper industry, industrial dipentene is a mixture of different terpenes with very low price. Its major components are monoterpenes including isomers of limonene (**1**), terpinenes (**2–4**), terpinolene (**5**) and other menthadienes (**6** and **7**), all bearing the chemical formula of $C_{10}H_{16}$. With its huge output, industrial dipentene can serve as a natural and renewable feedstock for fine chemical industries. Various and vast oil-based raw materials can be thus produced starting from this green resource.

Owing to the similarity of the molecular structure, *p*-cymene (**8**) is the most promising and valuable product obtained by the dehydrogenation of industrial dipentene. It is an important and valuable intermediate in the flavor and fragrance industry. *p*-Cymene can be oxidized to *p*-cresol or 4-isopropylbenzaldehyde under different oxidation conditions. It is also the building block for synthesis of non-nitrate musk such as tonalide. Moreover, *p*-cymene is used as solvent, heat transfer medium and masking odor for industrial products as well.

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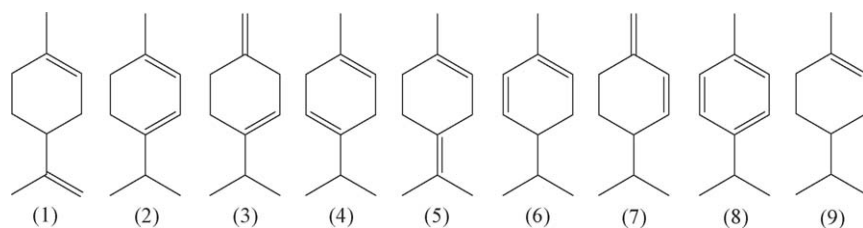
Generally, *p*-cymene can be produced by Friedel-Crafts alkylation of toluene with propylene or 2-propanol. But hazardous acid catalysts such as $AlCl_3$ or HF are required for good performance of this reaction, which raise the problems of handling, safety, corrosion and waste disposal. Zeolite-based catalysts have been introduced to overcome these drawbacks [3–9]. However, significant amounts of by-products such as *n*-propyltoluene, *m*- and *o*-cymene were formed over different zeolites according to the geometry and architecture [4,5,7–9].

So the alternative method to produce *p*-cymene by dehydrogenation of terpenes showed its great advantage of high activity and shape selectivity. Several papers concerning different catalysts such as nickel, palladium on coal or alumina, platinum on coal, chromium oxide with or without oxides of copper or zinc, Fuller's earth, copper–nickel, activated alumina, and the heteropolyacid $H_5PMo_{10}V_2O_{40}$, have been published [1]. Among them, Hölderich group has made a special effort and achieved remarkable progress in the research of hetero-geneous catalytic transformation from terpenes to *p*-cymene [10–14]. Yet, most of their studies were based on the noble metal Pd.

In this paper, the conversion of industrial dipentene over Al- and Zn-containing mesoporous molecular sieves is investigated. The effects of acidic sites on catalytic activities are also discussed. SBA-15 is chosen as the catalyst support in consideration of its large pore size, high surface area and hydrothermo-stability. For comparison, the catalytic property of MFI type zeolite HZSM-5 is also tested.

2. Experimental

2.1. Catalyst preparation

SBA-15 was synthesized according to the reference using triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) as organic template [15]. In a typical procedure, 8.0 g P123 (MW = 5800, Aldrich) was dispersed in 60.0 g water and 240 g 2 M HCl solution at 313 K, followed by the addition of 17.0 g of tetraethylorthosilicate (TEOS) as the silica source with stirring. The mixture was continuously stirred at 313 K for 24 h, then transferred to a Teflon-lined autoclave and submitted to a hydrothermal process at 373 K for another 24 h. After cooling to room temperature, the solid products were filtered, washed and dried at room temperature in air. For the removal of the template, calcination was carried out at 823 K in air for 5 h. The calcined SBA-15 was then used as carrier of the catalysts.

An impregnation method was introduced to load Al and Zn on SBA-15. $Al(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were selected as precursors of aluminum and zinc elements, respectively. The precursors were dissolved in deionized water at a concentration that depended on the desired metal loading. A certain amount of SBA-15 was dispersed into the above solutions by ultrasonic vibration, and then the mixture was evaporated and dried thoroughly at room temperature. After impregnation, the acquired powders were calcined at 823 K for 5 h again to get the final catalysts. These catalysts are denoted as Al/SBA-15(x) and Zn/SBA-15(x), respectively, where x is the molar ratio of Si to the loaded metals. K-modified Al/SBA-15 samples were also obtained by re-impregnation of potassium carbonate solution on calcined Al/SBA-15(26), with following calcination as well. These samples are named KAl/SBA-15(26,y), where y is the ratio of Al to K.

HZSM-5 was prepared from the commercially available NaZSM-5 (Nankai University, Si/Al = 25) by ion exchange method according to a report [16].

2.2. Catalysts characterization

The catalysts were analyzed by XRF to determine the elemental compositions on a Bruker S4 Explorer using Rh as anode target material, while the optimum test settings were predefined in SPECTRA^{PLUS}.

XRD patterns were recorded with a Bruker D4 powder X-ray diffractometer, which employed Ni-filtered Cu Kα radiation and was operated at 40 kV and 40 mA. The scanning range of small-angle pattern was from $2\theta = 0.5–5°$, step size 0.01°, and the range of wide-angle was from $2\theta = 5–60°$, step size 0.02°.

The nitrogen adsorption/desorption isotherms at 77 K were measured using a Micromeritics Tristar 3000 system. The pore structural data were analyzed by the BJH (Barrett–Joyner–Halenda) method using the Halsey equation for multilayer thickness. The pore size distribution curve came from the analysis of the adsorption branch of the isotherm.

The prepared samples were also observed by TEM (JEOL JEM2011); this instrument was fitted with an energy-dispersive X-ray emission analyzer (EDX). The amorphous character of the catalysts was verified by selected-area electron diffraction (SAED). The samples were supported on carbon-coated copper grids for the experiment.

^{27}Al MAS NMR spectra were recorded at room temperature on a Bruker MSL-300 spectrometer with a resonance frequency of 78.21 MHz. The magnetic field was 7.05 T. The spin rate of the sample was 4.0 kHz and the number of scans was 4000–