

In situ infrared study of *n*-heptane isomerization over Pt/H-beta zeolites

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Abstract

The isomerization of *n*-heptane over hydrogenated (H-) and Pt-loaded (Pt/H-) beta zeolites was observed directly by in situ infrared spectroscopy for investigation of the reaction mechanism and coking process. Carbonaceous species produced in the reaction are identified as either highly branched polyolefins (1485 cm⁻¹ band) or coke (1600 cm⁻¹). The former can be readily removed by O₂ treatment at moderate temperatures (>573 K), whereas complete removal of the latter requires higher temperatures (>723 K). The formation of coke is successfully inhibited by the presence of H₂ in the reaction stream. The hydrogenation and dehydration functionality of Pt particles in this catalyst system has been confirmed through H/D isotope exchange experiments.

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1. Introduction

A fundamental problem in heterogeneous catalysis research is the difficulty in performing in situ measurements of the reaction system. Such measurements involve monitoring the reactants in the gas stream under appropriate temperatures and pressures. It is accepted that characterization results obtained under working conditions provide invaluable information for understanding the reaction process. Despite great efforts in recent years to identify the active sites of catalysts and elucidate the reaction mechanism by in situ spectroscopy, further application of the spectroscopic approach has been hindered by the lack of suitable spectroscopic cells and the complexity of data analysis [1].

Among various characterization techniques used to date, in situ infrared (IR) spectroscopy has attracted much attention, particularly for the zeolite and zeolite/adsorbate systems, as a facile and sensitive technique for studying zeolite acidity, the nature of adsorbed species, and the interaction between reactants and catalysts [2]. In situ nuclear magnetic resonance

(NMR) analysis, another powerful characterization method, suffers quenching problems and thus is limited in the range of applicable temperature. In contrast, in situ IR can be used over a broad temperature range, from temperatures suitable for the study of cryogenic interaction between probe molecules (e.g., CO or N₂) with zeolite acidity to those of industrial processes, often above 573 K [3,4]. Some interesting applications of in situ IR spectroscopy have been reviewed recently [5].

The isomerization of *n*-heptane over Pt-loaded beta zeolites has become more important as the demands for octane-enhancement processes have increased. The catalytic isomerization of *n*-heptane, with a research octane number (RON) of zero, into more valuable products, such as mono-branched isomers (42–65 RON) and multibranched isomers (80–112 RON) using a solid catalyst remains an important research topic in industrial refinement [6]. In the isomerization process, *n*-heptane is converted in the presence of H₂ to suppress catalyst deactivation and increase the yield of desired branched products. Matsuda et al. recently examined various catalysts in *n*-heptane isomerization and found that Pt/H-beta zeolite catalyst exhibited the most promising catalytic performance of those tested, possibly due to the unique structure of three-dimensional interconnected channels of BEA-type zeolite [7]. With respect to the mechanism of action, it has been suggested that the skele-

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tal isomerization of alkanes proceeds over Pt/zeolites through a bifunctional reaction mechanism involving Pt-catalyzed dehydrogenation of alkane to alkene and reversible hydrogenation of alkene to alkanes, where the acidity of the zeolites promotes protonation of the intermediate alkene and subsequent rearrangement [8]. But recent experiments have cast doubt on this model, suggesting instead that the reaction is initiated solely by Brønsted acidity through carbocation, and that the Brønsted acidity facilitates subsequent rearrangement while Pt catalyzes alkene hydrogenation [9].

Various characterization methods have been applied to investigate this reaction system [10,11]; however, there are no reports of in situ IR studies of *n*-heptane isomerization over beta zeolites, despite the advantages of such a sensitive vibrational spectroscopy technique in gaining a more comprehensive understanding of the reaction mechanism. As Pt/beta zeolite catalysts are increasingly used for selective catalytic reduction of NO_x with hydrocarbons, knowledge of the intrinsic properties of Pt/H-beta zeolite is expected to aid the understanding of other reactions [12].

The present work used in situ IR spectroscopy to study the isomerization of *n*-heptane over H/beta zeolite and the Pt/H-beta zeolite catalyst in the high-temperature reactant stream (to 723 K). The investigation focuses on the inhibition of coke formation by the presence of H₂ and the role of Pt particles in the isomerization process.

2. Experimental

2.1. Catalyst preparation

NH₄-beta zeolite (Si/Al = 25) was kindly provided by Zeolyst (USA). H/beta zeolite was prepared by calcination of NH₄-beta zeolite at 773 K for 5 h. The Pt/H-beta zeolite catalyst was prepared by a conventional aqueous ion-exchange method involving the addition of 5 g of NH₄-beta zeolite to 100 mL of dilute aqueous tetraammineplatinum(II) chloride [Pt(NH₃)₄]Cl₂ solution containing 25 mg of Pt. The solution was stirred vigorously at 373 K for 12 h to promote the ion-exchange reaction. The resultant ion-exchanged zeolite was filtered and washed thoroughly with deionized water at room temperature before being dried at 343 K overnight. The dried sample was heated from 273 to 773 K at a rate of 0.5 K min⁻¹ and then held at the maximum temperature for 5 h. (This slow heating rate was applied to avoid the agglomeration of Pt species and to obtain a good dispersion of Pt particles on the catalyst surface.) Inductively couple plasma optical emission spectroscopy (ICP-OES) confirmed that the catalyst was loaded with 0.5 wt% Pt, as expected. Experience indicates that NH₄-beta zeolite is a better precursor for the ion exchange than H-beta zeolite in terms of dispersion.

2.2. Catalytic reactions

The catalytic isomerization of *n*-heptane was carried out in a U-shaped fixed-bed quartz tube reactor under atmospheric pressure. The catalyst bed was supported in the center of the reactor

by quartz wool. Gas flow rates were controlled by mass flow controllers, and the reactor was heated in a furnace. *n*-Heptane was introduced by syringe pump to the reaction feed at a H₂-to-*n*-heptane molar ratio of 5. The contact time (W/F) of *n*-heptane was approximately 3 g h mol⁻¹. The catalyst was reduced under H₂ at 673 K for 1 h before reaction. The reaction products were monitored by gas chromatography (Shimadzu GC-12A) with an ID Petrocol™ DH fused silica capillary column and flame ionization detector. The product selectivity reported herein is based on the carbon mass balance.

2.3. In situ IR characterization

The in situ IR cell used to investigate the reaction mechanism at elevated temperature and pressure is shown in Fig. 1. The cell was fabricated from stainless steel and included two CaF₂ windows in Teflon holders sealed by Kalrez O-rings [13,14]. Four KBr windows were placed inside the cell to minimize dead space, allowing the IR cell to operate as a microreactor with an optical path length of ca. 2 mm. The sample holder was fixed in the center of the cell, with gas inlet and outlet ports located on opposite sides to guarantee exposure of the catalyst sample to the pretreatment gas or reactants. A thermocouple was set in contact with the sample wafer to monitor the cell temperature. The gas inlet port was connected to a gas flow controlled by mass flow controllers, and the gas outlet port was connected to the gas chromatograph for detection of the reaction products. The tubing of the reaction system was heated throughout the reaction, to avoid condensation of heavy product molecules and thereby guarantee complete detection. Such an in situ cell is expected to be suitable for reactions at temperatures up to 773 K and pressures up to 1 MPa. The present measurements were carried out at atmospheric pressure.

Approximately 10 mg of the catalyst was pressed into a self-supporting wafer and mounted in the center of the cell for reaction and IR measurement. All IR spectra were recorded on a Fourier transform (FT) IR spectrometer (JASCO 7300) fitted with a mercury-cadmium-telluride (MCT) detector. The resolution of the spectrometer was 4 cm⁻¹ over 64 scans. Before measurement, the wafer was heated at 673 K under H₂ for 1 h to reduce the catalyst and desorb water. The sample was then cooled to the desired reaction temperature and exposed to the flow of H₂/*n*-heptane or He/*n*-heptane at a molar ratio of 5. The flow of H₂ or He was maintained at 6.4 mL min⁻¹ during IR measurements, which were performed in the reactant atmosphere.

H/D isotope exchange experiments were conducted to investigate the role of Pt particles in the isomerization process. In these experiments, the proton in the zeolite was replaced with deuterium and D₂ was used in place of H₂ as the feed gas. The catalyst, either H-beta or Pt/H-beta zeolite, was first reduced under 50% H₂/He (60 mL min⁻¹) at 673 K for 2 h, and then exposed to 50% D₂/He (60 mL min⁻¹) at 673 K for a further 1 h. After the catalyst was cooled to the desired reaction temperature (498–573 K), the sample cell was purged with pure D₂ (60 mL min⁻¹) for 30 min. The sample was then exposed to

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