n-Heptane hydroisomerization over Pt/MFI zeolite nanosheets: Effects of zeolite crystal thickness and platinum location

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ABSTRACT

Platinum was supported on MFI-type (ZSM-5) zeolites with various crystal thicknesses ranging from 300 to 2 nm (i.e., from bulk crystal to nanosheet). Two series of Pt/MFI were prepared by the ion exchange of $Pt(NH_3)_4^{2+}$ and the impregnation of colloidal Pt nanoparticles. The ion exchange yielded Pt nanoparticles that were supported inside zeolite pores, whereas the impregnation yielded Pt nanoparticles supported exclusively on the external crystal surfaces. The two series of Pt/MFI were used as catalysts for the hydro-isomerization of n-heptane to investigate the effects of zeolite crystal thickness and Pt location. This research showed that the product selectivity to branched isomers could be significantly improved by decreasing zeolite crystal thickness to nanosheets. The selectivity improvement was attributed to short diffusion path lengths for branched products to escape before cracking.

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1. Introduction

Liquid n-alkanes are important precursors for transportation fuels that can be obtained from petroleum distillation, Fischer–Tropsch synthesis, and bio-oil deoxygenation [1]. However, such linear hydrocarbons have poor fuel properties (e.g., low octane numbers in gasoline) that require additional refining processes. Selective hydroisomerization is a well-known process for improving the fuel quality of n-alkanes by converting them into branched isomers [2–4]. A typical catalyst for this process is bifunctional, consisting of a noble metal (e.g., Pt or Pd) dispersed on an acidic support. The metal component catalyzes the generation of intermediate olefins via dehydrogenation and the formation of products via hydrogenation. The acidic sites are responsible for generating carbenium ions from olefins for isomerization [4]. Among the catalysts developed so far, Pt-loaded aluminosilicate zeolites are widely used in commercial processes due to their strong acidity, high metal dispersion, and shape-selective micropores [2–4]. However, the presence of uniform micropores (<2 nm) in micrometer-sized crystals often imposes slow mass transfer, leading to low

catalytic efficiency during reactions. Continuous efforts have been devoted to overcome this diffusion limitation and to improve the catalytic process [5–7].

Diffusion in zeolites can be improved by shortening the diffusion path lengths via the synthesis of nanocrystalline zeolites or by the generation of mesopores within a zeolite crystal. Zeolites resulting from both approaches have been investigated in n-alkane hydroisomerization reactions in the past. For example, Chica and Corma supported Pt nanoparticles (NPs) on nanocrystalline beta zeolite of ∼30 nm in diameter [8]. Additionally, De Jong and Koningsberger supported Pt on mordenite zeolite after the generation of mesopores [9,10]. There are other studies employing various methods to generate mesopores in zeolites [11–14] and to delaminate zeolite into nanosheets [15]. These zeolite catalysts, supporting Pt metals, exhibited significant improvements of selectivity in n-alkane hydroisomerization compared to bulk zeolite. Thus, small zeolite crystal sizes were paramount to improve branched hydrocarbon selectivity.

The location of Pt metal is important in bifunctional catalysts. Since the introduction of the bifunctional concept by Weisz [16], it has been suggested that the metal and acid sites should be as near as possible for high catalytic activity and selectivity [17]. In this respect, methods to support Pt NPs uniformly, such as the ion-exchange (IE) technique, are widely used in the preparation of bifunctional Pt/zeolite catalysts [18]. There are some cases in which Pt NPs and acid catalytic sites are bifunctional without close

contact. In these cases, the rapid transfer of reaction intermediates via surface or gas-phase diffusion is known to allow the kinetic coupling between two detailed catalytic processes over a distance, leading to a sequential bifunctional pathway [19]. Numerous attempts have been made to understand the distance effects using a physical mixture of individual catalytic components such as Pt/SiO_2 and acidic zeolite. Often, the Pt catalyst is supported on non-acid silica, while the acid components are located in the zeolite particles [16,20–22]. The metal-to-acid site distances are not precisely controlled in this case. The distance between Pt and the acid would be more precisely controlled if Pt NPs could be supported on the external surfaces of a zeolite particle with a well-defined thickness. It would therefore be interesting to try a series of acidic zeolites with extremely well-defined crystal sizes over a wide range, decreasing the crystal thickness down to only a few nanometers.

Owing to the development of zeolite synthesis strategies using zeolite structure-directing surfactants, ultrathin zeolite nanosheets of a single unit cell thickness can now be synthesized ($\sim$2 nm) [23–25]. This has provided the opportunity to extend the investigation of zeolite crystal size on n-alkane hydroisomerization selectivity down to the 2-nm scale. Zeolite nanosheets with well-defined thicknesses can support Pt NPs inside the internal micropores following the IE method. It is also possible to support Pt NPs exclusively on the external surfaces of the nanosheet using the colloid impregnation (CI) method [26,27]. In the CI method, Pt NPs of uniform diameter are prepared in a colloidal solution. This solution is then impregnated into a porous material. The NPs can maintain their original particle diameters after the impregnation, unless the supported particle concentration is high enough to cause agglomeration. The Pt NP diameter can now be controlled over a wide range (1–100 nm) [28]. If NPs larger than 1.5 nm are used, these NPs can be exclusively supported on the external crystal surfaces of zeolite because they are too large to enter zeolite micropores ($\sim$0.55 nm).

The present work was undertaken to investigate the effects of single-unit-cell-sized zeolite crystal thickness and Pt location in relation to acid sites on linear alkane hydroisomerization. To address these points, we synthesized conventional ZSM-5 with approximately 300-nm crystal thickness, nanocrystalline MFI ($\sim$10 nm), and MFI nanosheets with 2-nm thickness along the b-axis. To support Pt NPs on these zeolites, we used two different preparation methods: conventional IE and the recently developed CI. The supported Pt catalysts were characterized by hydrogen chemisorption and transmission electron microscopy (TEM). The catalytic performance of these Pt-supporting zeolites for hydroisomerization was investigated using n-hexane (n-C_6) and n-heptane (n-C_7) as substrates, reflecting the importance of upgrading light naphtha components [8]. The investigation was focused on n-C_7, due to its higher tendency to crack than n-C_6 [29]. The result of the catalytic investigation was analyzed in terms of zeolite crystal thickness and Pt location.

2. Experimental

2.1. Zeolite preparation

2.1.1. Zeolite synthesis

The 2-nm thick MFI zeolite nanosheets were synthesized using a compound with a molecular formula of $C_{16}H_{33}$–$N^+(CH_3)_2$–C_6H_{12}–$N^+(CH_3)_2$–$C_6H_{13}(Br^-)_2$ [$C_{16-6-6}(Br)_2$] as a structure-directing agent (SDA), following a procedure described previously [24]. In brief, water glass with a Si/Na ratio of 1.75 was used as the silica source, and sodium aluminate was used as the alumina source. The molar composition of the starting mixture was 100 SiO_2:1 Al_2O_3:7.5

$C_{16-6-6}(Br)_2$:30 Na_2O:24 H_2SO_4:4000 H_2O. The mixture was heated in a Teflon-lined autoclave with tumbling in an oven at 413 K for 7 d. The zeolite product was collected after filtration, washing with water, and drying at 373 K. The zeolite thus obtained was calcined at 823 K in air. The zeolite was ion-exchanged three times with 1 M NH_4NO_3 solution and subsequently calcined again at 823 K for its full conversion to the H^+ form. This sample is denoted "NS-2" in the text.

Nanocrystalline MFI zeolite of $\sim$10 nm was synthesized with a diammonium-type SDA, C_3H_7–$N^+(CH_3)_2$–C_6H_{12}–$N^+(CH_3)_2$–C_3H_7 ($Br^-)_2$ [$C_{3-6-3}(Br)_2$] following the procedure reported by Na et al. [30], except the synthesis temperature (423 K) and the starting molar composition (100 SiO_2:0.083 Al_2O_3:10 $C_{3-6-3}(Br)_2$:30 Na_2O:15 H_2SO_4:6000 H_2O). The zeolite was also converted to the H^+ form in the same manner used for NS-2. This zeolite is denoted by "NC-10" in the text.

Bulk zeolite with an approximately 300-nm crystal thickness was obtained with tetrapropylammonium hydroxide (TPAOH). The starting mixture had a molar composition of 100 SiO_2:1 Al_2O_3:30 TPAOH:3 H_2SO_4:6000 H_2O. Tetraethylorthosilicate (TEOS, 95%, Junsei) was used as the silica source, and aluminum sulfate [$Al_2(SO_4)_3\cdot18H_2O$, 98%, Sigma–Aldrich] was used as the alumina source. In a typical synthesis, 0.67 g of $Al_2(SO_4)_3\cdot18H_2O$ was dissolved in 114 g aqueous TPAOH solution (5.4 wt.%). To this solution, 20.8 g of TEOS was added with magnetic stirring. The mixture was heated to 333 K, and stirring was continued for 6 h. The sol-like clear mixture was heated in a Teflon-lined autoclave at 443 K for 2 d under static conditions. The resultant zeolite product was collected and treated in the same manner as for NS-2. This sample is denoted as "B-300" in the text, which means "bulk crystals with 300-nm thickness".

A commercial MFI zeolite in the NH_4^+ form was purchased from Zeolyst (CBV8014, SiO_2/Al_2O_3 = 80) and calcined at 823 K before use. The zeolite was composed of aggregated nanosize crystals with a wide distribution of thicknesses from 20 to 50 nm (see Section 3.1 for detailed characterization). This sample is designated as "C-40" in the text, where "C" means "commercial" and "40" stands for its mean crystal thickness.

2.1.2. Platinum loading

The IE method was applied in the following manner [31–33]. Briefly, 1.0 g of zeolite was added to a 20 mL aqueous solution containing 0.0202 g of $Pt(NH_3)_4(NO_3)_2$ (98%, Sigma–Aldrich). The slurry was magnetically stirred overnight at room temperature. Afterward, the zeolite was filtered, washed with deionized water, and dried at 373 K. The zeolite powder was placed on a fritted disk inside a Pyrex U-tube flow reactor, heated to 623 K at a ramping rate of 0.4 K min^{-1}, and kept at this temperature for 2 h under flowing dry oxygen (>1 L min^{-1} g^{-1} zeolite). The activated sample was treated in flowing H_2 (>200 mL min^{-1} g^{-1}) with linear heating to 573 K for 4 h and holding for 2 h. The sample was subsequently degassed at 573 K for 2 h to remove chemisorbed hydrogen.

The CI method was used in the same manner as reported by the Somorjai group [26], except for the use of octylamine (99%, Sigma–Aldrich) as an organic-capping agent. Pt NPs exhibiting a particle size distribution of 1.4 ± 0.3 nm (see Section 3.1) were prepared by adding an ethylene glycol solution of NaOH (10 mL, 0.5 M) to a 10 mL ethylene glycol solution containing 0.2 g of H_2PtCl_6 (37.5 wt.% Pt, Heesung Metal) [34]. The mixture was heated at 413 K for 3 h under vigorous stirring with N_2 bubbling. The resultant dark-brown colloidal solution was mixed with 1.23 mL of octylamine (N/Pt molar ratio of 20) dissolved in toluene (15 mL). Ethanol was added to this mixture to provide a homogeneous colloidal solution. Fifty milliliters of deionized water was added to this solution, and the solution was mixed by shaking. The colorless aqueous layer was discarded, and the organic layer containing the