



Gd/HZSM-5 catalyst for conversion of methanol to hydrocarbons: Effects of amounts of the Gd loading and catalyst preparation method

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ABSTRACT

In this work, the effect of the gadolinium (Gd) content and preparation method on the characteristics of Gd-modified HZSM-5 catalysts and their reactivity in a methanol-to-hydrocarbons (MTH) reaction has been studied in detail. Gd/HZSM-5 catalysts with Gd contents of 1 wt% (1GdHZ), 5 wt% (5GdHZ), and 10 wt% (10GdHZ) were prepared by an incipient wet impregnation method, and another Gd-modified HZSM-5 catalyst (GdHZ_IE) was prepared by an ion exchange method. It was found that increasing the Gd content in the catalysts prepared via the impregnation method with uniformly distributed nano-sized particles and thin films of Gd₂O₃ directly influenced the crystallinity, surface area, pore volume, acid-base properties, and reactivity of the catalysts. In particular, the amount of Lewis acid sites (LAS) on the catalyst determine the selectivity of light olefins and aromatics during the MTH reaction. In contrast, the GdHZ_IE catalyst possess a larger number of strong LAS and show higher aromatic selectivities compared with the bare HZSM-5 catalyst. Regardless of the preparation method, the catalyst modification by Gd inhibited the formation of polycondensed aromatic species on the catalyst surface and reduced the amount of carbon deposition by more than 50%. As the increasing amounts of Gd reduced the amount of carbon deposition, the lifetimes of the Gd/HZSM-5 catalysts were also prolonged.

1. Introduction

Owing to the presence of high-density acid sites on their surfaces and the property of shape selectivity, zeolite-based solid acid catalysts have been used for naphtha cracking since the 1950s. They are now widely used as cracking catalysts throughout the petrochemical industry [1–3]. Zeolite-based catalysts have also been employed in a variety of processes related to carbon-resource conversion because of their inherent chemical and physical properties [3–7]. Recently, the process of converting methanol into value-added hydrocarbons (methanol-to-hydrocarbons, MTH) such as light olefins or aromatics over solid acid catalysts has been studied extensively in an effort to develop a sustainable energy source [4,5]. Methanol can be mass-produced from synthesis gas (CO + H₂), which is produced by coal gasification or reforming methane and biomass. The Fischer-Tropsch (FT) process enables direct conversion of synthesis gas to hydrocarbons and even though the MTH process requires one more step than the FT process, the high selectivity for the target product emanating from the use of

zeolite catalysts offsets the shortcomings of the MTH process [4,8].

The ZSM-5 zeolite is a highly active catalyst and is used to produce hydrocarbons, especially aromatic compounds, from methanol because of its strong acid sites and unique pore structure [5,9,10]. However, carbocation intermediates formed during the MTH reactions are readily adsorb on the strong acidic sites of zeolite catalysts and form polycondensed aromatics consisting of several benzene rings via a sequence of growth mechanisms. This eventually results in the blocking of active sites, pore mouths, and intersections in the zeolite catalyst (so-called “coking”) [7,11–14]. Thus, despite the high activity and selectivity of the zeolite catalysts, this severe deactivation from coking is a major problem for their application in commercial MTH plants.

The acid sites are typically located on the surface and in the pores of the zeolite, and they are also the active sites for the MTH reaction and responsible for the excellent reactivity of the catalyst. The hydrocarbon intermediates or cations produced during the reaction are readily and strongly adsorbed onto these sites [15,16]. The once-adsorbed hydrocarbon intermediates on the surface and/or in the pores of the zeolite

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catalysts grow as aromatic carbon compounds via oligomerization, hydrogenation and dehydrogenation, cyclization, and aromatization; on a surface without any restrictions on their growth, poly-condensed aromatics can cover the active sites or pore openings, and even block the zeolite pores from inside to disturb the diffusion of reactants into the active sites [12,13,15,17]. As a result, the diffusion and contact of the reactant with the active sites on the surface and those located in the pores are intrinsically blocked, and the zeolite catalyst rapidly becomes inactive.

Various methods have been used to try to diminish the rapid deactivation of the ZSM-5 zeolite catalysts by carbon deposition. One of these methods involves the synthesis of nano-sized or hierarchically structured zeolite crystals by an alkali treatment or bottom-up synthesis in order to improve the diffusivity of the reactants to the active sites [18–21]. In this case of morphological modification, the deactivation of ZSM-5 zeolite catalysts by pore clogging is reduced and the lifetime of the catalyst is thereby increased. However, the increase in the diffusion and surface area by zeolite structure control does not reduce the rate and amount of carbon deposition [17]. Another strategy to improve catalyst deactivation by coke formation is to reduce the amount of acid sites, especially Brønsted or Lewis acid sites, by either increasing the Si/Al ratio during zeolite synthesis or via ion exchange with metal cations to prevent the adsorption of the hydrocarbon intermediates formed during the reaction [17,22,23]. Although this method has a clear effect in terms of prolonging the catalyst lifetime, the catalytic activity of the zeolite simultaneously decreases owing to the reduced number of acid sites. Therefore, this method is not useful for reactions that require a catalyst with highly acidic active sites.

Yet another method to prevent catalyst deactivation by coke formation during the MTH reaction is to modify the ZSM-5 zeolite catalyst with a small amount of metal acting as a coke inhibitor. Noble metals such as platinum and gold have been shown to catalyze the hydrogenation of ZSM-5 catalysts by interfering in the formation of condensed aromatics or graphite coke [24–26]. The use of rare earth metals for the same purpose has also attracted interest because of their relatively low cost and abundance. A Gd-promoted ZSM-5 catalyst has recently been shown to have excellent anti-coking abilities for chemical conversion of hydrocarbons. Kim and co-workers have recently found that the adsorption of carbocations and formation of complex aromatics structured coke is impeded during hydrocarbon cracking and methanol conversion reactions on the modified ZSM-5 catalyst surface on which Gd₂O₃ is present uniformly in the form of nano-sized particles or thin films, which improves the lifetime of the catalyst [27–29]. Nevertheless, the use of Gd metal as a coke inhibitor still needs to be studied for a deeper understanding into its mechanism. Hence, in this work, the changes in the physicochemical properties of the Gd/HZSM-5 catalysts and the catalytic activities in a MTH reaction were studied according to the different Gd loading amounts and the preparation method.

2. Experimental

2.1. Catalyst preparation

The Gd/HZSM-5 catalysts were firstly prepared by an incipient wet impregnation method. NH₄-ZSM-5 (Zeolyst CBV 5524G, Si/Al = 25) was calcined in a muffle furnace under the flow of air at 600 °C for 6 h to prepare HZSM-5. Gd precursor (Gd(NO₃)₃·6H₂O, Sigma-Aldrich) satisfying ca. 1 wt%, 5 wt%, and 10 wt% of the Gd content was dissolved in de-ionized water, which amount is slightly above the pore volume of the HZSM-5, and the solution and HZSM-5 were mixed and stirred well. The Gd/HZSM-5 catalysts, denoted as 1GdHZ, 5GdHZ, and 10GdHZ, were finally obtained after dry at 110 °C for overnight and calcination at 550 °C for 5 h.

The Gd/HZSM-5 catalyst was also prepared by ion exchange method. The prepared HZSM-5 was added into 0.15 M of aqueous solutions of Gd precursor with a ratio of 50 (mL_{solution}) to 1 (g_{HZSM-5}). Ion

exchange was accomplished under stirring at 80 °C for 12 h, and the slurry was washed by de-ionized water, dried at 110 °C overnight. After three subsequent ion exchange processes, a final calcination step was performed in air for 5 h at 550 °C to remove any residual precursor salt materials and oxidize the active metals. The obtained samples was denoted as GdHZ_IE, the bare HZSM-5 was denoted as HZ for comparison.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was assigned to identity peak shape and relative crystallinity for the prepared Gd/HZSM-5 catalysts. A Rigaku D/MAX IIIIB X-ray diffractometer equipped with Cu-Kα radiations was used for bulk phase analysis. All spectra were collected at 2θ values between 3° and 80° using a step size of 0.02° and 2 s per step.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out to measure the Gd loading using an iCAP 6500 (Thermo Scientific)

N₂ adsorption-desorption analysis was carried out using TriStar 3000 (Micromeritics) at a temperature of –196 °C. Before the adsorption-desorption measurements, all of the Gd/HZSM-5 catalysts were degassed at 300 °C under 1.0 × 10^{–6} Torr for 4 h.

Scanning electron microscopy (SEM) images of the Gd/HZSM-5 catalysts were obtained using a Zeiss Ultraplus Thermal Field Emission Scanning Electron Microscope.

Scanning transmission electron microscopy (STEM) imaging and energy dispersive X-ray spectroscopy (EDS) analysis were conducted using a TalosTM F200S transmission electron microscope (FEI), which at 200 kV provides a nominal probe size of < 0.12 nm.

Temperature programmed desorption of ammonia and carbon dioxide (NH₃-TPD & CO₂-TPD) were performed on an Autochem II 2920 of Micromeritics instrument. Before the TPD analysis, all the catalysts were pretreated at 600 °C with flowing He gas for 1 h in order to remove any adsorbed water and saturated with NH₃ gas (15%, balanced with He, flow rate: 50 mL/min) or CO₂ gas (10%, balanced with He, flow rate: 50 mL/min) for 30 min at a temperature of 100 °C. After the saturation stage, the catalysts were purged with flowing He gas for 1 h to remove weakly adsorbed NH₃ or CO₂ molecules on the surface. Finally, TPD measurement was carried out with maintaining a ramping rate of 10 °C/min from 100 °C to 600 °C with flowing pure He gas.

Brønsted (BAS) and Lewis acid sites (LAS) were determined via pyridine adsorption-desorption experiments in a stainless steel variable temperature gas flow transmission cell using a Fourier transform infrared (FT-IR) spectrometer equipped with a Mercury-cadmium-telluride-B detector (Nicolet Nexus 4700). 30 mg of the powder catalyst samples were prepared as self-supporting pellets with a diameter of 12 mm and placed in the cell. After pre-treatment at 250 °C to remove adsorbed water, pyridine vapor was introduced into the cell from a saturator with flowing pure He gas at 150 °C for 20 min. Then, pure He gas was purged through the catalyst pellet at 150 °C for 3 h to remove any physically adsorbed pyridine molecules prior to the collection of the IR spectra. The IR spectra of adsorbed pyridine molecules on the surface of the catalyst were recorded from 1400 cm^{–1} to 1700 cm^{–1}, and both chemisorbed pyridinium ion (PyH⁺) on Brønsted acid sites and pyridine bonded on Lewis acid sites (PyL) were quantified at 1545 cm^{–1} and 1455 cm^{–1}, respectively. The extinction coefficients were taken to be 1.13 cm^{–1}mmol^{–1} (PyH⁺) and 1.28 cm^{–1}μmol^{–1} (PyL), respectively for estimation of acid sites [30]. The quantity of BAS and LAS were calculated from the formula presented below (Beer–Lambert's law):

$$C = \frac{A}{\epsilon} \times \frac{S}{m} \times 1000$$

where C is the concentration of acid sites (μmol g^{–1}), A is the area of band (cm^{–1}), S is the surface of the wafer (cm²), ε is the molar extinction coefficient (cm μmol^{–1}), and m is the mass of sample (mg).

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