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Article

Enhancing hydrothermal stability of nano-sized HZSM-5 zeolite by phosphorus modification for olefin catalytic cracking of full-range FCC gasoline



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ABSTRACT

In this study, phosphorus modification by trimethyl phosphate impregnation was employed to enhance the hydrothermal stability of nano-sized HZSM-5 zeolites. A parallel modification was studied by ammonium dihydrogen phosphate impregnation. The modified zeolites were subjected to steam treatment at 800 °C for 4 h (100% steam) and employed as catalysts for olefin catalytic cracking (OCC) of full-range fluid catalytic cracking (FCC) gasoline. X-ray diffraction, N₂ physical adsorption and NH₃ temperature-programmed desorption analysis indicated that, although significant improvements to the hydrothermal stability of nano-sized HZSM-5 zeolites can be observed when adopting both phosphorus modification strategies, impregnation with trimethyl phosphate displays further enhancement of the hydrothermal stability. This is because higher structural crystallinity is retained, larger specific surface areas/micropore volumes form, and there are greater numbers of surface acid sites. Reaction experiments conducted using a fixed-bed micro-reactor (catalyst/oil ratio = 4, time on stream = 4 s) showed OCC of full-range FCC gasoline—under a fluidized-bed reaction mode configuration—to be a viable solution for the olefin problem of FCC gasoline. This reaction significantly decreased the olefin content in the full-range FCC gasoline feed, and specifically heavy-end olefins, by converting the olefins into value-added C₂–C₄ olefins and aromatics. At the same time, sulfide content of the gasoline decreased *via* a non-hydrodesulfurization process. Nano-sized HZSM-5 zeolites modified with trimethyl phosphate exhibited enhanced catalytic performance for OCC of full-range FCC gasoline.

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1. Introduction

Hydrothermal stability is one of the most important properties that influence the application of zeolitic catalysts. It is well-known that the hydrothermal stability of a zeolitic material depends mainly on its topological structure and framework silica-to-alumina ratio (SAR). However, hydrothermal stability

is also significantly influenced by zeolite crystal size. Typically, large-pore zeolites possessing low SARs and nano-particle sizes have poor hydrothermal stability. Conversely, small- and medium-pore zeolites having high SARs and large crystal sizes have improved hydrothermal stability. Although the unique medium-pore MFI structure and high-silica framework composition gives ZSM-5 zeolites excellent hydrothermal stability,

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efforts to further enhance ZSM-5 hydrothermal stability are certainly meaningful for practical uses, especially when subjecting nano-sized ZSM-5 to harsh hydrothermal conditions to applications such as fluidized catalytic cracking (FCC), where the catalyst is required to withstand steaming treatment at >700 °C. Several techniques have been developed hitherto for enhancing zeolite hydrothermal stability. For example, rare earth ion exchange [1–3], dealumination and silicon-addition by $(\text{NH}_4)_2\text{SiF}_6$ modification [4,5], and high-temperature steam calcination [6–8] are applied to low silica type zeolites such as X and Y. Additionally, phosphorus modification by H_3PO_4 , $(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$ impregnation has been proposed for high SAR zeolites, such as β and ZSM-5 [9–13]. Multiple strategies are available for improving the hydrothermal stability of low SAR zeolites. However, few approaches are known for high SAR zeolites. As for ZSM-5 zeolite, phosphorus modification with H_3PO_4 , $(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$ does not always result in satisfactory improvement to hydrothermal stability, and there are few published reports detailing hydrothermal stability enhancement of nano-sized ZSM-5 zeolites.

Gasoline obtained from FCC processes account for a major proportion of the Chinese gasoline pool and generally contains high sulfide and olefin content. To conform to international gasoline standards, the China V gasoline standard has been issued to meet the necessary specifications and will be implemented in 2017. Stringent threshold levels governed by the China V gasoline standard state that the sulfur content should be ≤ 10 $\mu\text{g/g}$, and olefin content ≤ 24 vol.%. Therefore, China has a long-term requirement to upgrade FCC gasoline by decreasing sulfide and olefin content. Currently, the ‘S-zorb’ process configured within a fluidized bed reactor has been accepted by many large-scale refineries for FCC gasoline desulfurization. In this process, the sulfides in FCC gasoline are removed by selective adsorption over a selective adsorbent. Thereafter, the adsorbent is regenerated to recover the adsorption capacity. The ‘S-zorb’ process is efficient for the deep desulfurization of FCC gasoline. However, it is unaffordable for smaller refineries. Therefore, hydrodesulfurization will continue to be an important alternative to the ‘S-zorb’ process. There already exist several well-known hydrodesulfurization processes for FCC gasoline, such as ‘SCANfining’ and ‘Prime G+’. Although these processes are able to simultaneously reduce sulfide and olefin content, hydrodesulfurization usually suffers from relatively big research octane number (RON) loss owing to the hydrogenation saturation of olefins. This problem is of concern in the case of deep hydrodesulfurization. Additionally, the removal of extra olefins from FCC gasoline *via* hydrogenation is too expensive because of considerable H_2 consumption.

In previous studies [14–16], we introduced a fixed-bed olefin-to-aromatics (OTA) reaction using modified nano-sized ZSM-5 zeolites to reduce olefin content in full-range FCC gasoline. The transformation of olefins into aromatics *via* the OTA reaction was considered as an alternative solution to the olefin problem of FCC gasoline, as aromatics have a higher RON rating than olefins, and the process does not require the consumption of H_2 if the FCC-OTA gasoline is not hydrodesulfurized down-stream. However, the economic viability of the OTA reac-

tion being implemented within industry is limited because of low OTA conversion and fast catalyst deactivation when set-up in a fixed-bed operation mode. Further potential restrictions will arise if future legislated threshold levels of aromatics in gasoline are lowered. For these reasons, we are now interested in studying the viability of olefin catalytic cracking (OCC) of full-range FCC gasoline with nano-sized ZSM-5 zeolites when configured within a fluidized-bed. The objective is to efficiently transform the extra olefins in FCC gasoline into value-added short-chain olefins like ethylene, propylene and butenes, and to direct the FCC-OCC gasoline for further hydrodesulfurization treatment. Employing nano-sized ZSM-5 zeolites as the catalyst is likely to benefit OCC of full-range FCC gasoline by enhanced performance, however, it is important to improve the hydrothermal stability of nano-sized ZSM-5 zeolites, suitably for fluidized-bed configuration, as if the crystal size is ultrafine the inherent stability of the ZSM-5 structure will weaken.

Therefore, this study is two-fold: first, enhancing the hydrothermal stability of nano-sized ZSM-5 zeolites by a novel phosphorus modification route featuring trimethyl phosphate and, second, the evaluation OCC of full-range FCC gasoline when employing the stabilized zeolite catalysts under fluidized-bed configuration.

2. Experimental

2.1. Catalyst preparation

Nano-sized NaZSM-5 powder (20–50 nm, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$) was supplied by Dalian Ligong Qiwangda Chemical Technology. First, the received zeolite was calcined in a muffle furnace in the presence of static air to remove the organic template. Thereafter, the template-free zeolite was treated by a conventional ammonia ion exchange method to obtain HZSM-5. Further modification of the zeolite was performed by introducing 0.2 wt.%, 0.6 wt.%, 1.0 wt.%, 2.0 wt.%, and 3.0 wt.% phosphorus into the HZSM-5 zeolite by incipient wet impregnation *via* an aqueous solution of trimethyl phosphate ($(\text{CH}_3)_3\text{PO}_4$) at room temperature. For the purpose of comparison, the same phosphorus modifications were repeated with ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). The modified catalysts were denoted as 0.2P(Z)–3.0P(Z) for $(\text{CH}_3)_3\text{PO}_4$ -modified zeolites, and 0.2P(Y)–3.0P(Y) for $\text{NH}_4\text{H}_2\text{PO}_4$ -modified analogues. To investigate changes to hydrothermal stability of HZSM-5 zeolites as a function of phosphorus content and type, the phosphorus-modified catalysts were further steam treated at 800 °C for 4 h (100% steam). The steamed samples were given a “-st” postfix to the original catalyst codes. All catalysts were pressed, crushed and sieved to 40–60 mesh sizes for reaction purpose.

2.2. Characterization

Chemical composition of the catalyst samples was analyzed using a Bruker SRS 3400 X-ray fluorescence (XRF) spectrometer. X-ray diffraction (XRD) was performed using a Rigaku D/MAX-2004 diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 100

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