Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Aromatization over nanosized Ga-containing ZSM-5 zeolites prepared by different methods: Effect of acidity of active Ga species on the catalytic performance

Q1 Yujun Fang, Xiaofang Su, Xuefeng Bai, Wei Wu*, Gaoliang Wang, Linfei Xiao, Anran Yu

National Center for International Research on Catalytic technology, Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, Heilongjiang, China

ARTICLE INFO

Article history:
Received 16 January 2017
Revised 17 March 2017
Accepted 22 March 2017
Available online xxx

Keywords:
Nanosized ZSM-5 zeolite
Isomorphous substitution
Impregnation
Active gallium species
Aromatization

ABSTRACT

Nanosized Ga-containing ZSM-5 zeolites were prepared via isomorphous substitution and impregnation followed by characterized using various techniques. The catalytic performance of the zeolites for the aromatization of 1-hexene was investigated. The results indicate that isomorphous substitution promotes the incorporation of Ga heteroatoms into the framework along with the formation of extra-framework GaO^+ species ($[GaO^+]^a$) that have stronger interactions with the negative potential of the framework. In addition, based on the Py-IR results and catalytic performance, the $[GaO^+]^a$ species with stronger Lewis acid sites produced a better synergism with moderate Brønsted acid sites and thus improved the selectivity to aromatic compounds. However, the impregnation results in the formation of Ga_2O_3 phase and small amounts of GaO^+ species that are mainly located on the external surface ($[GaO^+]^b$), which contribute to weaker Lewis acid sites due to weaker interactions with the zeolite framework. During 1-hexene aromatization, the nanosized Ga isomorphously substituted ZSM-5 zeolite samples (Ga*x*-NZ5) exhibited better catalytic performance compared to the impregnated samples, and the highest aromatic yield (i.e., 65.4 wt%) was achieved over the Ga4.2-NZ5 sample, which contained with the highest Ga content.

Q2

1. Introduction

According to the Worldwide Fuel Charter (fifth edition), the excess octane-boosting olefins (50–65 vol%) in fluid catalytic cracking (FCC) gasoline may be related to environmental pollution, such as photochemical smog (i.e., ozone) that is caused by a mixture of olefins and NO_x, a high concentration of toxic compounds (i.e., CO) in exhaust due to deficient combustion of olefins and fine particulate matter in the air [1,2]. The high content of olefin also leads to uneven atomization, reducing the performance of automobile engines. The coke in automobile engines can also be caused by olefin instability in FCC gasoline [3]. Moreover, FCC gasoline contains very high amounts of sulfur-containing compounds, which originate from the heavier oil fractions used in FCC reactors that must be removed by hydrodesulfurization processing [4]. The restrictions on the olefin and sulfur content in gasoline have become more stringent to meet the requirement of the Euro 5 regulation (olefin $\leq$ 18 vol%, sulphur $\leq$ 10 ppm), and this requirement will be even lower in the future. In addition to removing sulfur, hydroprocessing, hydrogenates a portion of the present olefins, which reduces the octane number (RON) of the FCC gasoline [5]. Aromatization of the residual olefins and paraffins is a high-efficiency way method for producing high value-added and high-energy aromatic compounds (low benzene content) as octane boosters, which significantly reduce the olefin content in FCC gasoline and ensure high octane number [6–8]. The urgent need for light aromatic compounds with extensive application has stimulated interest in investigating hydrocarbon aromatization. The separated excess aromatic compounds as primary raw materials can be widely used in the synthetic petrochemicals and fine chemical products. Furthermore, aromatic-enriched gasoline is an ideal additive composition that is typically blended with the hydrocarbon pool product to form the final gasoline product.

The strong acidity of ZSM-5 zeolites promotes coke deposition and leads to deactivation of catalysts. Ga-containing ZSM-5 zeolites are highly efficient bifunctional catalysts for converting olefins to aromatics and have been widely used in propane, LGP and methanol aromatization [9–12]. The incorporation of gallium into the ZSM-5 zeolite not only reduces the Brønsted acid strength but also results in the formation of additional stronger Lewis acid sites due to the extra-framework Ga species which can improve the rate-determining dehydrogenation step of olefin aromatization.

* Corresponding author.
E-mail address: wuwei@hlju.edu.cn (W. Wu).

http://dx.doi.org/10.1016/j.jechem.2017.03.014
2095-4956/

Moreover, the routes for preparing Ga-containing zeolites affect the nature and location of the Ga species in zeolites.

In previous studies, a simple impregnation method for Ga-incorporation was adopted, and the nature of the active gallium species was investigated. Ausavaukhi et al. [13] prepared a series of Ga-containing ZSM-5 zeolites via impregnation and physical mixing and determined that the GaO^+ species act as stronger Lewis acid sites. Xiao et al. [14,15] also reported that the extra-framework GaO^+ species in impregnated ZSM-5 samples can react with the acidic protons of the zeolite framework and contribute to a strong Lewis acidity, which is favorable for dehydrogenation during propane aromatization under a N_2 atmosphere. Rodrigues et al. [16,17] studied the nature and activity of gallium species for the aromatization of propane under H_2 and concluded that the reduced gallium species, which were obtained via hydrogen reduction of GaO^+ species (GaH_2^+), in the impregnated ZSM-5 zeolites serve as the actual active sites for propane activation. Therefore, to promote the formation of more active Ga species with a high dehydrogenation activity, several methods have been developed (e.g., reduction/oxidation cycles, acid impregnation and treatment with steam), and the results indicate that samples modified via these approaches produced higher aromatic yield [14–19]. Recently, Lai et al. [20,21] adopted an optimized combination of mesostructuring and Ga impregnation to increase the GaO^+ concentration in ZSM-5 channels and promote the outward diffusion of products, which was beneficial for methanol conversion to aromatic compounds.

However, the blockage of micropores was inevitable, and the increase in active Ga species was limited for samples prepared via the impregnation method. To find the optimal route for Ga-incorporation, Yassir et al. [22] investigated three different methods including direct in-situ synthesis, aqueous impregnation and ion-exchange to prepare microsized Ga-containing ZSM-5 zeolites. In this study, the Ga-substituted ZSM-5 sample that was obtained via direct synthesis exhibited the highest activity for propane and butane aromatization due to the presence of highly dispersed, reducible, extra-framework Ga species in close proximity to the zeolitic Brønsted acid sites. However, the type of Ga species in the prepared samples and the relationship between the Lewis acid strength and the extra-framework Ga species were not discussed. Moreover, this study was primarily focused on microsized zeolites rather than nanosized zeolites which may have promising applications. In comparison to microsized zeolites, nanocrystalline zeolites exhibit better mesoporosity and possess improved accessibility to internal acid sites, which may overcome the diffusion limitation of the reactants, intermediates and products [23,24].

In this work, nanosized ZSM-5 and Ga isomorphously substituted ZSM-5 zeolites (Ga-substituted ZSM-5) were successfully synthesized using an in-situ seed-induced method [25]. However, in contrast to our previous study, the seed suspension was prepared using a high-efficiency microwave irradiation heating method that promoted the uniform nuclear and saved time. For comparison, Ga-modified nanosized ZSM-5 zeolites (Ga/NZ5) with the same Ga content as Ga-substituted ZSM-5 zeolites were prepared via a conventional impregnation method. The two series of zeolites exhibit entirely different interface properties and compositions. The relationship between the Lewis acid strength and the active Ga species with different locations in ZSM-5 zeolites and two series of Ga-containing ZSM-5 catalysts was investigated. To the best of our knowledge, this relationship is rarely investigated. All of the samples were characterized using several physicochemical technologies to systematically demonstrate the relationship between the acidity and the Ga species in the two series of catalysts prepared via impregnation and isomorphous substitution. 1-hexene was used as the feedstock in olefin aromatization to study the dehydrogenation activity of the Ga species located in different positions with different acidities. In addition, further comparisons were focused on the stability of the catalysts and catalyst deactivation due to coke deposition.

2. Experimental

2.1. Preparation of catalyst

Nanosized ZSM-5 and Ga-substituted ZSM-5 zeolites were synthesized via an in-situ seed-induced method. The seed suspension was prepared from a mixture of aluminum isopropoxide (AIP), tetrapropylammonium hydroxide (TPAOH, 25% in water), tetraethylorthosilicate (TEOS), and deionized water with a molar ratio of $1Al_2O_3$: $100SiO_2$:36TPAOH:$1083H_2O$. Then, the suspension was crystallized via microwave irradiation heating at 140 °C for 0.5 h. After the dissolution of $NaAlO_2$ and Ga_2O_3 in a NaOH solution, Ludox (30% SiO_2 in water) was added to the mixture followed by the addition of a 5 wt% seed suspension without purification. The molar composition of the synthesis gel was $1Al_2O_3$:nGa_2O_3:$100SiO_2$:$12Na_2O$:$2500H_2O$ ($n = 0.625$, 1, 2.5). The gel was transferred to a Teflon-lined stainless steel autoclave and hydrothermally crystallized at 180°C for 16 h. The synthesized samples in H-form after ion-exchange with a 1 mol/L NH_4NO_3 solution and calcination at 550 °C for 3 h are referred to as Ga*x*-NZ5, where *x* represents the mass percent content of Ga.

The nanosized ZSM-5 zeolite was synthesized using the same method that was employed for the Ga*x*-NZ5 samples except for the addition of a Ga source. This sample is referred to as HNZ5. The Ga impregnated zeolites were prepared via an incipient wetness impregnation method with a $Ga(NO_3)_3$ solution followed by calcination at 550 °C for 3 h, and these samples are referred to as Ga*x*/NZ5, where *x* represents the mass percent content of Ga.

2.2. Characterization of catalyst

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance diffractometer using Cu *Kα* ($\lambda = 1.5404$ Å) irradiation. The integration of the peak areas of 22.0°–25.0° for the HNZ5 zeolite was defined as 100%. The chemical compositions of the zeolites were determined using X-ray fluorescence (XRF) spectroscopy on a Bruker SRS-3400 instrument. The Ga content of the samples was determined using an inductively coupled plasma spectrometer (ULTIMA 2, ICP-OES). The scanning electron microscopy (SEM) was performed on Hitachi S-4800 microscope. The transmission electron microscopy (TEM) images were recorded using a JEM-2100 microscope. An Autosorb-1-MP apparatus (Quantachrome Instruments) was used to characterize the surface area and pore volume via N_2 adsorption-desorption at 77 K. The ^{29}Si, ^{27}Al and ^{71}Ga MAS NMR spectra were measured on a Bruker Avance-400 spectrometer using a 4 mm zirconia rotor with a spin rate of 10, 12 and 10 kHz, respectively.

The H_2 temperature-programmed reduction (H_2-TPR) was performed on an AutoChem II 2920 Chemisorption Analyzer apparatus (Micromeritics Instruments). Approximately 200 mg of the sample was placed under argon for 1 h at 40 mL/min and 500 °C for pretreatment. Then, the sample was cooled to room temperature and subjected to pulses of a 10% H_2/Ar gas mixture at a constant heating rate of 20 °C/min until adsorption saturation at 900 °C. The amount of gallium oxide was measured by calculating the hydrogen consumption. X-ray photoelectron spectroscopy (XPS, Kratos, ULTRA AXIS DLD) was performed with Al *Kα* ($h\nu = 1486.6$ eV). The C (*1s*) peak at 284.6 eV was referenced for calibration of the binding energies. The NH_3-TPD profiles were measured at a constant heating rate of 15 °C/min in a 40 mL/min flow of argon. These measurements were carried out on a device equipped with a thermal conductivity detector. The Py-IR spectra were recorded on a

Please cite this article as: Y. Fang et al., Aromatization over nanosized Ga-containing ZSM-5 zeolites prepared by different methods: Effect of acidity of active Ga species on the catalytic performance, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.03.014