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Hydrothermal stability of MTT zeolite in hot water: The role of La and Ce

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ABSTRACT

Stability of catalysts under steam and hot water environment is a crucial issue in upgrading of water-containing feedstocks such as biomass and heavy oil. The hydrothermal stability of MTT zeolite in hot water under autogenous pressure was investigated at 473 K. The effect lanthanum (La) and cerium (Ce) on the hydrothermal behavior of MTT zeolite were also studied under the same condition. The parent MTT zeolite, as well Ce and La modified zeolites showed remarkable stability in hot water. Minimal losses in textural properties originated from the hydrolysis of Si—O—Si and Si—O—Al bonds in the zeolite framework. The study shows the potential of the MTT zeolite as a catalyst for biomass conversion and heavy oil upgrading.

1. Introduction

Zeolites have been used in hydrothermal reactions such as aquathermolysis of heavy oil [1], steam catalytic cracking [2], and biomass processing like aqueous reforming and the hydrolysis of simple and complex sugars [3–7]. Water has been singled out over other ionic liquids for the aforementioned processes due to its abundance, cheapness and its ability to dissolve oxygenates in the case of biomass processing. Zeolites are being implemented for these reactions due to their non hazardous nature and also the simplicity of separating catalyst after completing the reaction [8]. Therefore, having a good insight into the hydrothermal behavior and stability of zeolites is of high significance.

The hydrothermal stabilities of zeolites such as ZSM-5 (MFI), SAPO-11 (AEL), and zeolite (FAU) in hot water have been reported [8,9], to mention but a few. Recently, we reported the steam catalytic cracking of *n*-hexane on MTT and La modified MTT zeolite [10], where both MTT and La-MTT zeolite showed excellent stability in the steam catalytic process at 923 K for 8.5 h. However, recent studies reported that reasonable stability in steam environment is different than hydrothermal stability in hot water. For instance, faujasite-based catalysts relatively is stable in steam to some extent, but readily collapse and undergo structural changes in hot water [8,11]. Hence, investigating the stability of zeolite in both hot water and steam gives a better understanding on hydrothermal stability zeolite-based catalysts.

The hydrothermal stability of MTT zeolite in hot water, to the best of our knowledge, is yet to be investigated. MTT (ZSM-23) zeolite is a one dimensional, 10 membered ring (10-MR) zeolite with excellent isomerization ability and a potential catalysts for numerous acid-catalyzed hydrocarbon conversions such as selective cracking of light naphtha to propylene, steam catalytic cracking, and methanol-to-hydrocarbon [10,12,13].

In order to comprehend the usability of MTT zeolite in hydrothermal severe reactions, there is a need to study its stability in hot water as a guide. Herein, we report our findings on the hydrothermal stability of MTT zeolite as well as La and Ce exchanged MTT zeolites in hot water under autogenous pressure at 473 K (200 °C).

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2. Experimental

2.1. Hydrothermal synthesis of MTT zeolite

MTT zeolites were synthesized in accordance to our previous reports with a certain adaptation [12,14,15]. Instead of using a microwave, synthesis was carried out in a rotating (tumbling) autoclave. To synthesize MTT zeolite ($SiO_2/Al_2O_3 = 150$), 0.31 g sodium hydroxide (BDH chemicals) was dissolved in 43.96 g de-ionized water and 0.25 g of $Al_2(SO_4)_3 \cdot 18H_2O$ (Jassen Chimica) was added to form an aluminate solution. The solution was stirred vigorously and 6.17 g of isopropyl amine (Acros organics) was added. A 9.31 g of 40% colloidal silica (Sigma Aldrich, AS-40) was then added and the whole mixture was vigorously stirred for 30 min. Thereafter, the solution was transferred into a PTFE autoclave vessel for hydrothermal treatment at 453 K with a tumbling speed of 50 rpm for 48 h. The resulting zeolite was centrifuged and washed several times with de-ionized water and then dried at 393 K for 12 h. Thereafter, calcination of the dried zeolite powder was carried out at 823 K for 12 h to get organic-structure directing agent (OSDA) free zeolite.

The resulting MTT zeolite prepared as described above was then exchanged with NH_4OH (Techno pharmachem) solution according to our previous reports to get the H-form of the zeolite.

2.2. Ion exchange of MTT zeolite with La and Ce

Lanthanum and cerium exchanged MTT zeolite were prepared by exchanging parent MTT zeolite with lanthanum nitrate hexahydrate (Merck) and ammonium cerium (IV) sulfate dihydrate (Sigma Aldrich). In a typical protocol to prepare La or Ce exchanged MTT zeolite, metal precursor with 2 wt.% metal content with respect to zeolite mass was dissolved in 20 mL de-ionized water. After, 1.8 g of parent MTT zeolite was added and the resulting mixture was treated under microwave irradiation at 358 K for 20 min. The resulting zeolite was centrifuged, washed several times with de-ionized water and then dried at 373 K for 12 h. Finally, dried zeolite powders were then calcined at 823 K for 12 to get metal exchanged zeolites.

2.3. Hydrothermal stability test

Hydrothermal stability test (HST) of parent MTT, La-MTT and Ce-MTT zeolites were done in water using a PTFE lined steel autoclaves at 473 K in a range 12–72 h. Liquid to solid mass ratios of 30 and 60 were used. After hydrothermal treatment in water, samples were dried for 16 h at 393 K and thereafter calcined for 2 h at 823 K.

2.4. Sample designation

After completing the hydrothermal stability test, samples were designated as H-MTT-*x*, La-MTT-*x* and Ce-MTT-*x*. Where x ($x = 0$, 12, 36 and 72 h) represents the time for the hydrothermal stability test. Samples with liquid to solid mass ratio of 60 were designated with an addition 60 in a square parenthesis, for instance H-MTT-72 [60].

2.5. Sample characterization

XRD analysis of parent H-MTT samples, La-modified samples, Ce-modified samples and all hydrothermally treated samples were measured on a Rigaku Miniflex II diffractometer in the 2θ range of 5–50°. Morphology of samples was done using FESEM (TESCAN). Physisorption properties of samples were carried out using an ASAP 2020 porosimeter (Micromeritics). In the physisorption process, N_2 was employed as probing molecule. The positions of Si and Al in the framework were studied using ^{27}Al and ^{29}Si MAS NMR. Solid-state ^{27}Al MAS NMR spectra of samples were conducted on a JEOL ECA-600 spectrometer at a resonance frequency of 156.4 MHz with a 4 mm sample rotor spinning at a rate of 15 kHz. The ^{29}Si MAS NMR spectra were measured using a JEOL ECA-400 spectrometer at a frequency of 399.0 MHz via a 6 mm sampling rotor at a spinning rate of 5.5 kHz.

3. Results and discussion

3.1. Effect of La and Ce as modifier on H-MTT zeolite

The XRD patterns of parent H-MTT, La-MTT and Ce-MTT zeolites are shown in Fig. 1. The prepared H-MTT zeolite showed excellent crystallinity and diffraction peaks matching with MTT (ZSM-23) zeolite framework [12,14–16]. We observed that the addition of both La and Ce metals via an ion exchange protocol did not result in any changes in diffraction patterns of the MTT framework. In addition, the crystallinity of the MTT zeolite structure was preserved. The peaks of lanthanum oxide or cerium oxide were not observed. Furthermore, FESEM analysis (see Fig. 2) of parent H-MTT, La-MTT and Ce-MTT zeolites reveal the peculiar rod-like structures of the MTT zeolite crystals [14,16]. The addition of both La and Ce to the MTT framework did not result to changes in crystal morphology and the diffraction pattern as observed in FESEM and XRD analysis respectively.

Another interesting observation is the metal content of La and Ce modified MTT zeolites observed by XRF analysis. Table 1 shows the XRF elemental analysis of H-MTT, La-MTT and Ce-MTT zeolite. The Si/Al of parent H-MTT zeolite increased from 64 to 69 and 70 in Ce-MTT and La-MTT zeolites, respectively. The increase in Si/Al ratio after ion exchange suggest that the ion exchange of La and Ce was not limited to only the proton present on the zeolite, but also with Al. Furthermore, the exchange ability of H-MTT with Ce was found to be about three times greater that of La. The increase in Si/Al ratio suggests that dealumination might have occurred during the ion exchange procedure. Further probe by ^{27}Al NMR analysis clearly indicated the presence of dealumination during the ion exchange protocol. Fig. 3a shows the ^{27}Al NMR spectra of parent-MTT, La-MTT and Ce-MTT zeolite samples. All samples contained a major peak at 55 ppm for tetrahedral coordinated framework aluminum and octahedral coordinated extra framework Al (EFAL) at 0 ppm [17]. We observed a clear reduction in the peak intensities at 55 ppm for both La-MTT-0 and Ce-MTT-0 zeolites in the order H-MTT-

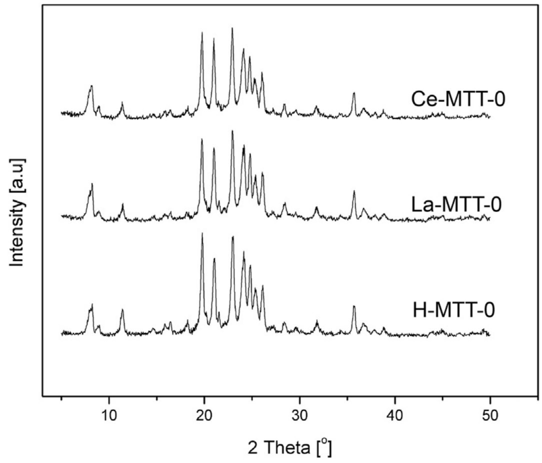

Fig. 1. XRD pattern of parent H-MTT-0, La-MTT-0 and Ce-MTT-0 zeolites.