High Performance of H₃BO₃ Modified USY and Equilibrium Catalyst with Tailored Acid Sites in Catalytic Cracking

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Abstract

Increasing the cracking ability of catalyst by adjusting its surface acid property is of great significance for oil refining industry. The effects of boric acid on the structure and surface acidity of ultra stabilized Y (USY) and FCC equilibrium catalyst during the modification were investigated. The structural and surface properties of the prepared samples were characterized by low-temperature N₂ sorption, XRD, ²⁷Al and ²⁹Si MAS NMR, and FTIR using pyridine probe molecule. Modified USY and equilibrium catalyst possessed reduced Lewis acid sites. The Brönsted/Lewis acid ratios of USY increased from 0.64 to 1.56 after modification, at the same time, the microporous surface areas increased, due to the nonframework and framework dealumination during the modification. The catalytic cracking tests were performed on a bench-scale micro reactor at 500°C and atmospheric pressure, using n-dodecane as a modeling reactant and vacuum gas oil as conventional feedstock. The results showed that

modified samples with high Brönsted acid sites had better cracking abilities and increased hydrogen transfer activity than raw samples.

Keywords: Zeolite Y; Boric acid; Brönsted acid; Catalytic Cracking; Modification

1. Introduction

Fluid catalytic cracking (FCC), which deals with the conversion of heavy crude oils into light fuels and chemicals in the presence of a solid acid catalyst, is still a key process in the modern refining scheme[1, 2]. The amounts of the most valuable products formed in the FCC process, such as gasoline, liquefied petroleum gas (LPG), light olefins, and diesel, are determined by feed composition, operating conditions, and the catalyst property. An industrial FCC catalyst is a classical solid acid catalyst and typically consists of an active component embedded in an amorphous matrix, a binder, filler and some additives. The main active component is faujasite Y that amounts to 10-50% in FCC catalyst but provides most of the cracking activity. Y-type zeolite has the three-dimensional 12-membered ring channels of 0.74 nm diameter and is composed of cubooctahedral sodalite cages linked together to form the supercage of 1.3 nm. The excellent catalytic activity of protonic Y-type zeolite is ascribed to two main properties: the strong Brönsted acidity of bridging Si-(OH)-Al sites in the presence of Al inside the framework and the shape selectivity effect due to the particular framework topology with well-defined pore size and structure. In contrast, other components of FCC catalyst are mainly composed of clay, alumina or aluminosilicate which possess lower acidity and catalytic activity compared to Y-type zeolite and fulfill both physical and catalytic

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functions for big molecule pre-cracking.

It is well known that both Brönsted and Lewis acid sites on the FCC catalysts play important roles in catalytic cracking of hydrocarbons. Extensive research efforts show that Brönsted acid sites, mainly generated by the tetrahedral Al^{3+} of zeolite framework, are the prime active sites for the catalytic cracking reactions in hydrocarbon conversion[3-6]. In contrast, Lewis acid sites are thought to be the actives for thermal cracking and/or dehydrogenation instead of catalytic cracking reaction. This raises the question of serious coking and high dry gas yields which is unfavorable in industrial applications [2, 7, 8]. From this, Brönsted acid site is probably the more efficient and friendly active site for hydrocarbon conversion[3]. Zeolite properties can be tailored or carefully selected according to the requirements of practical application under consideration. However, the controllable adjustment of the acid properties such as the acid amounts, acid strength, and the possible synergies among Brönsted and Lewis acid sites is still a challenge and it has been one of hot issues in the research and development of FCC catalyst in last two decades[9].

To accurately control the acid properties, various strategies such as doping with rare earth ions[10, 11], controlling of crystal size [12, 13], and modulating silica to alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$)[1, 14, 15], have been extensively studied. Additionally, acid properties can also be directly adjusted by optimizing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the formulation of raw material in the crystallization synthesis of Y; however, this method is limited by the synthetic conditions. For doping Y with rare earths, an increase in the percentage of rare earths generally gives rise to an increase in feed conversion accompanied by an undesirable decrease in the octane number of gasoline. In reality, zeolite catalysts are frequently pretreated in various ways such

as steaming, to increase the activity and selectivity. Y-type zeolites, usually with relatively high Si/Al ratios (H-Y) and frequently stabilized by dealumination (ultra-stable Y, USY), are among the most relevant solid acids for their industrial applications. In this process, hydrothermal treatment is a convenient procedure to extract Al from Y framework as well as create additional mesoporous channels above 6 nm which are in favor of the cracking of big molecules [16, 17]. By this method, the number of acid centers decreases, but the acidity of remaining centers rises up to a degree. However, it should be carefully performed considering the severe damage to zeolite crystallinity due to excessive framework dealumination[18]. Besides, Lewis acid featured Al fragments that are taken off from the framework will plug the micropores causing a fast deactivation of FCC catalyst. So, it is a challenge to generate mesopores on Y zeolite while keeping its high crystallinity.

In our previous studies, various acid agents such as phosphoric acid, citric acid, and ammonium fluosilicate have been employed to adjust the acid properties and textural properties of Y and USY[19-22]. However, an obvious drawback of acid treatment is the great reduction of crystallinity probably due to the high acid strength of these modifiers. In our recent research, it was found that the amount of Lewis acid site of γ -Al₂O₃ could be reduced using a mild inorganic acid (boric acid) as a modifier[3]. Additionally, the importance of acid sites in zeolite catalyzed conversion and the seeming simplicity of the reaction using alkanes/alkenes as reactants have led to a wide range of fundamental and applied studies to tailor the surface acidity and understand its effects on catalytic reactions [4, 6, 23-26].

The aim of this work is to develop USY and FCC equilibrium catalyst with tailored acid sites using boric acid as a mild modifier for the catalytic cracking of hydrocarbons and to

evidence the active sites involved in the reaction. Physical properties of materials such as crystalline structure, textural properties, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and surface acidity, were investigated using: X-ray diffraction (XRD), low-temperature nitrogen sorption, ^{27}Al and ^{29}Si magic angle spinning solid-state nuclear magnetic resonance (MAS NMR), and infrared spectroscopy (FTIR) with adsorption-desorption of probe molecules (pyridine). Catalytic cracking performances of modified samples were carried out in a bench-scale reactor under atmospheric pressure, at 500 °C, using n-dodecane as a modeling reactant and vacuum gas oil as conventional feedstock.

2. Experimental section

2.1 Raw Materials

Commercial USY product with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 9.35 (based on XRF analysis) was provided from Zibo Huaqing Powder Co. Ltd. Pseudoboehmite (Al_2O_3 content is 71.90 wt % on a dry basis) was provided by Sinopharm Chemical Reagent Co. Ltd. Equilibrium catalyst (commercially labeled as LVR-60R) was uploaded from a commercial FCC regenerator from vendor Petrochina Lanzhou Petrochemical Co. and marked as Ecat. Vacuum gas oil (VGO) was purchased from Fushun Petrochemical Co. Table 1 shows the properties of VGO and Ecat by the vendors. Other analytical reagents were purchased from Sinopharm Co. Ltd.

2.2 Modification of USY and equilibrium catalyst

USY was used as received and hydrothermally treated using H_3BO_3 as a modifier. Typically, 20.0 g USY was added into a three-neck flask of 100 mL deionized water and stirred at 80 °C by water bath heating. Then H_3BO_3 was added into the mixture. The above

suspension was stirred at 80 °C for 24 h. The final modified USY was obtained after filtration, cake drying, and calcination at 550 °C for 4 h at a heating rate of 3 °C/min. The samples were defined as X-USY, where X represents the mass ratios of H₃BO₃ to USY which were 2%, 5%, 10%, and 20%, respectively. On this basis, 20.0 g equilibrium catalyst (Ecat) was modified using 2.0 g H₃BO₃ following the procedure as described above. The modified sample was marked as M-Ecat.

To test the hydrothermal stability, all USY zeolites were hydrothermally aged at 800 °C with 100% water vapor for 4 h and correspondingly marked as X-USY-HT.

2.3 Modification of γ -Al₂O₃

Modified γ -Al₂O₃ was obtained by an improved sol-gel route as our previous report[3]. 21.25 g pseudoboehmite was dispersed in 50 mL of deionized water. Then 50 mL aqueous solution of 2.15 g of H₃BO₃ was added under vigorous stirring at 85 °C and followed by adjusting the pH value to 3.0 using 1.0 mol/L HNO₃ solution. The whole suspension was stirred vigorously at 85 °C for 6 h. Thereafter, aqueous ammonia was added dropwise into the solution to adjust the mixture to a pH of 6. The final sample was obtained after filtration of the quiescent suspension, cake drying and calcination at the same heating conditions. The H₃BO₃ modified γ -Al₂O₃ was marked as B-Al₂O₃. The same procedure was repeated using 2.50 g NH₄BF₄ instead of H₃BO₃ to obtain a NH₄BF₄ modified γ -Al₂O₃, marked as BF-Al₂O₃. In comparison, γ -Al₂O₃ was obtained by direct calcination pseudoboehmite under the same heating conditions.

2.4 Characterization

The crystalline structure and framework silica-to-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) were characterized by X-ray diffraction (XRD) on an X'Pert PRO MPD diffractometer (PANalytical B.V. Netherlands) with CuK-Alpha radiation ($k = 0.15418 \text{ nm}$), operating at 40 kV, 40 mA, and scanning from 5° to 75° at a speed of $0.01^\circ/\text{s}$. Eight characteristic peaks of USY zeolite ($2\theta = 15.64, 18.66, 20.36, 23.63, 27.04, 30.73, 31.79, \text{ and } 34.05$) were selected for calculating the relative crystallinity. The whole $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was detected by X-ray fluorescence (XRF) on an AXIOS-Petro instrument. The boron contents of all the samples were determined by the inductively coupled plasma – atomic emission spectrometry (ICP-AES) method according to the procedures of US EPA 6010C (2007). X-ray photoelectron spectroscopy (XPS) studies were done using ESCALAB 250Xi photoelectron spectrometer, using Al K α radiation from an X-ray source, and the base pressure in the analysis was kept at $5.0 \times 10^{-10} \text{ mbar}$. The binding energy positions were determined after subtraction of a simple Shirley-type background. Nitrogen sorption measurements at -196°C were carried out on a Micrometrics TRISTAR 3000 analyzer to characterize the textural properties. Prior to the measurements, the samples were outgassed at 300°C with a vacuum degree of 10^{-2} Torr for 3 h. The Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method were used to determine the surface area and pore volume of the samples. The relative pressures (P/P_0) for BET measurements were in the range of $0.07 - 0.30$, and the C (constant value) was about 20 ± 3 . ^{27}Al and ^{29}Si MAS NMR analysis of samples were performed on a Bruker Advance III 400 instrument at a resonance frequencies of 104.0 MHz . The Bruker 4.0 mm MAS detector was used for acquisition of 10

kHz MAS spectra. The single pulse sequence with RF-pulse duration of 0.3 μ s ($\pi/20^\circ$) and recycling time of 0.30 s was used.

The acid sites of all samples were detected on a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer using pyridine as a probe molecule. Each spectrum was recorded by a total of 64 scans with a resolution of 4 cm^{-1} . All samples were activated at 300 $^\circ\text{C}$ for 3 h before pyridine adsorption. Physically adsorbed pyridine on acid sites was removed by a vacuum molecular pump at 150 $^\circ\text{C}$ and $< 2 \times 10^{-3}$ Pa for 2 h.

2.5 Catalytic tests

Catalytic activity tests were performed in an automated bench-scale micro-activity test (MAT) unit with a tubular stainless steel reactor (inner diameter of 13 mm and length of 180 mm), which was designed according to ASTM D3907-80 standard [3]. The reactions were carried out at 500 $^\circ\text{C}$ for 75 s. 1.0 g X-USY or alumina sample was used with 1.0 g n-dodecane as feedstock while 4.0 g Ecat or M-Ecat sample was used with 1.0 g VGO as feedstock. The gases and liquid products were separated through ice water bathing and analyzed on a gas chromatography (Varian GC-3800) that had two TCD detectors and one FID detector. The conversion was defined as the weight percentage of converted n-dodecane. For VGO conversion, the liquid products were analyzed by gas chromatography simulated distillation and the mass percentages of gasoline (IBP-204 $^\circ\text{C}$), diesel (204-350 $^\circ\text{C}$), and slurry (> 350 $^\circ\text{C}$) in VGO conversion were qualified. The conversion was defined as the sum of the yields of dry gases ($\text{C}_1\text{-C}_2$), LPG ($\text{C}_3\text{-C}_4$), gasoline, diesel, and coke. An elemental analyzer (Elementar Vario EL III) measured the weight of coke deposited on the catalyst by

measuring the emitted CO₂ and CO in combustion. The maximum absolute error (< 4%) in the liquid yields was determined by triplicate experiments.

3. Results and discussion

3.1 Structural properties

The XRD patterns of modified samples are displayed in Figs. 1 and 2. Fig. 1a shows that all X-USY samples had the faujasite structure of Y zeolite and no other crystalline phases formed after H₃BO₃ modification. The relatively unchanged peak intensities indicated that there was no damage to the framework of modified USY. However, the peak positions shifted to higher 2θ angles with the increase of H₃BO₃ amounts, indicating that the unit cell sizes (*a*₀) became smaller after modification (Fig.1b). The calculated results from (331) and (533) lattice planes show that the framework SiO₂/Al₂O₃ ratios increased from 5.91 for USY to 10.47 for 20%-USY (Table 2). This change trend was consistent with the SiO₂/Al₂O₃ ratio change measured by XRF analysis. The Rietveld structure refinement results (Fig. S1) also showed that the unit-cell dimension in a-, b- and c-directions decreased linearly with the increase of boron contents in modified USY, indicating the cell shrinkage after modification. It could be attributed to the framework dealumination or the partial substitution of framework aluminum by boron which has a smaller atomic radius (0.82 for B atom and 1.18 Å for Al atom) during USY modification. However, the two characteristic bands at 1390 and ~940 cm⁻¹, which were regarded as the evidence of isomorph boron incorporation in zeolite framework, were not observed in all USY zeolites (Fig. S2)[27, 28]. It might be because the boron contents were low in the modified samples less than 3.57 wt.% detected by the ICP-AES)

method (Table 2).

Fig. 2a shows that all alumina samples had sole γ -Al₂O₃ phase indicative of no destruction of crystalline phase after modification by H₃BO₃ and NH₄BF₄. Fig. 2b shows that both Ecat and M-Ecat possessed both γ -Al₂O₃ phase and faujasite Y phase. No other crystalline phase was detected after H₃BO₃ modification. However, the peak positions of faujasite Y phase on M-Ecat shifted to higher degree, similar to those of modified USY.

NMR spectra can provide information about the coordination numbers of the atoms in USY zeolite. The signals of ²⁷Al and ²⁹Si MAS NMR spectra (Figs. 3 and 4) were first deconvoluted into separated peaks by using Gaussian function. Four resonance peaks are observed in ²⁷Al NMR spectra of USY (Fig. 3). The peak at ~60 ppm is assigned to framework tetra-coordinated Al (Al(IV)_a). The tail resonance peak at ~50 ppm, its assignment is unclear, can be marked as Al(IV)_b: (1) distorted tetra-coordinated framework Al atoms, (2) penta-coordinated aluminum species, and (3) non-framework tetra-coordinated Al species. The peaks at ~35 ppm and ~0 ppm are respectively attributed to penta-coordinated Al species (Al(V)) and extraframework hexa-coordinated Al species (Al(VI)). Obviously, the ratio of (Al(IV)) decreased after modification. Considering the SiO₂/Al₂O₃ ratio measured by XRF analysis in Table 2, the calculated results (Fig. 5a) show that the content of framework Al(IV) continuously decreased with the increase of H₃BO₃ usage, indicative of framework dealumination. Besides, the content of non-framework Al(VI) slightly decreased, probably due to the framework dealumination or the slow rate of the migration of non-framework Al species, which would be resolved in our next work.

Three types of Si-O-Al coordination states are observed in Fig. 4, depending on the number of Si atom connected to Al atom via bridged O atom. The peaks at -106, -101, and -94 ppm in turn correspond to silicon environments of $Q^4(\text{Si}(0\text{Al}))$, $Q^3(\text{Si}(1\text{Al}))$, and $Q^2(\text{Si}(2\text{Al}))$. Another weak shoulder peak at lower than -110 ppm can be assigned to $\text{Si}(4\text{Si})$ of the amorphous silica[22]. It has been recognized that the framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ could be calculated from the ^{29}Si NMR spectra besides XRD analysis [22, 29, 30]. It is interesting to note that, in Fig. 5b, there is an approximate linear correlation between the H_3BO_3 usage and framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios derived from NMR analysis, increasing slightly from 12.54 to 20.01. Note that the variation tendency of these $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios derived from both NMR analysis and XRD analysis was semblable. However, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio derived from NMR analysis was always larger than that from XRD analysis at the same H_3BO_3 usage, mainly because of the differences of analytical instruments and methods. No matter what, boric acid gave rise to framework dealumination of zeolite Y in the modification process accompanying with the reduction of crystal unit size a_0 (Fig.5 and Table 2).

3.2 Textural properties

Fig. 6a shows the N_2 sorption isotherms of USY samples. All samples exhibited IV-type isotherm curve and hysteresis loop. The high adsorptive quantity of nitrogen at low pressure ($P/P_0 < 0.1$) suggested the presence of micropore in zeolites. The adsorption isotherms gradually increased below $P/P_0 = 1.0$ and reached stable status at $P/P_0 = 1.0$, which was the capillary condensation of nitrogen vapor in the confined pores of samples. The narrow and long hysteresis loop suggested the characteristics of mesopores. The pore width distribution in Fig. 6b shows that the mesoporosity of modified USY varied little. All samples possessed the

bimodal mesopore distributions, which were the characteristic of hydrothermally treated commercial Y zeolites. Similarly, modified alumina and equilibrium catalyst showed few changes in their pore size distributions (Figs. S3 and S4).

Textural properties of all samples obtained from N₂ sorption curves in Table 2 show that modified USY had higher surface areas and pore volumes than raw USY. Specifically, 2%-USY had the highest surface area and pore volume. It was mainly attributed to the increased microporous surface area and microporous volume since the pH of modifying mixture was too weak ($\text{pH} \geq 3.0$) to create more mesopores. Nonframework Al³⁺ ions and Al³⁺ ions that were removed from framework would migrate out of zeolite pores, making the micropore more open and clearer. In this work, it is obvious that both nonframework and framework Al species decreased with the increases in H₃BO₃ usage in Fig. 5. Assuming no nonframework Al species were removed, the nonframework Al content in Fig. 5 would increase along with the framework dealumination indicating that non-framework Al species could be removed after modification but not “efficiently”. That is, low content of boric acid played an important role in cleaning micropores. However, higher H₃BO₃ amount inhibited the migration of aluminum species or combined with aluminium species to form new boron-oxygen-alumina species, giving rise to lower surface area and pore volume[3, 28, 31].

For alumina samples, B-Al₂O₃ had increased surface area while BF-Al₂O₃ had decreased surface area compared to -Al₂O₃. *It was due to the formation of aluminum-boron-oxo species in sole boric acid modification[32]. In contrast, fluorination reaction was found to be dominant with NH₄BF₄ modification in our previous report [3]. As a result, very little hydroxyl fluoride phase was formed which had the framework of a dense packed stacking*

[33]. In contrast, the surface area and pore volume of M-Ecat changed a little as compared to Ecat since it was a composite of USY and aluminosilicate matrix.

3.3 Surface acidity

Pyridine is an usual probe molecule, which can be absorbed by solid acid catalyst, to distinguish Brönsted acid site (BAS) and Lewis acid site (LAS). The spectra of pyridine adsorbed on USY is displayed in Fig. 7. Emeis et al.[34] had semi-quantitatively calculated the acid amount according to the IR band areas. The results calculated from Fig. 7a show that with the increase of H_3BO_3 amounts, the total acid amounts gradually decreased mostly due to substantial decrease of Lewis acid amount (Table 3 and Fig. 8a). In contrast, Brönsted acid amount increased and then decreased, with comparatively small amplitude. As a result, the Brönsted/Lewis acid ratios (BAS/LAS ratio in Fig. 8b) gradually increased with the increase of H_3BO_3 amounts, from 0.64 for USY to 1.56 for 20%-USY.

For USY zeolite, the hydroxyl groups on framework Si-O(H)-Al are the primary source of Brönsted acid site while the amorphous aluminum species are responsible for the Lewis acid site [35, 36]. H_3BO_3 modification partly removed the nonframework Al species out of the pore, improving the accessibility of framework hydroxyl groups. Therefore, the surface area and the amount of Brönsted acid site on modified USY increased. It is noted that the content of amorphous Al^{3+} species, i.e., nonframework Al species decreased less (Fig. 5a), but the amount of Lewis acid site decreased largely (Fig. 8a). It was probably attributed to the interaction between amorphous Al species and B atom. The XPS results (Fig. 9) showed that with the increases of H_3BO_3 usage, the Al content on the surface of modified USY rarely changed while the B content gradually increased. It indicated that the reduction of Lewis acid

amount was attributed to the removal of nonframework Al species and/or the coaction of nonframework Al species and boron.

Fig. 10 is the FTIR spectra of chemisorbed pyridine on modified alumina. The assignments of the characteristic bands with respect to acid sites in the spectra referred to the aforementioned parts. Compared to γ -Al₂O₃, the Lewis acid site of B-Al₂O₃ was remarkably reduced from 19.62 $\mu\text{mol}\cdot\text{g}^{-1}$ to 6.20 $\mu\text{mol}\cdot\text{g}^{-1}$ (Table 3). However, BF-Al₂O₃ possessed rich Brönsted acid site of 2.96 $\mu\text{mol}\cdot\text{g}^{-1}$ but similar amount of Lewis acid site compared to B-Al₂O₃. Both our previous work [3] and others' work [37-39] had proposed that the electron-withdrawing of μ_2 -OH by the strong electronegativity (3.98) of F atom in a pyrochlore-type structure of BF-Al₂O₃ was responsible for the appearance Brönsted acid sites, although no such crystalline phase was detected in XRD patterns. The results in Table 3 also show that the amount of Brönsted acid of M-Ecat slightly increased while the amount of LAS largely decreased compared with that of Ecat, bringing about the increase of BAS/LAS ratio from 0.55 to 1.17. Our results suggested that the acid sites on both alumina matrix and USY of equilibrium catalyst were tailored by H₃BO₃ modification.

It has been reported that the acid sites are predominantly located on corners and edges in the nanocrystals of aluminas [40]. It is also well-known that Brönsted acid sites in the form of hydroxyl groups often coexist with very strong Lewis acid sites of the Al³⁺ type on silica-alumina materials [41]. In other words, Brönsted acid site and Lewis acid site are interacted on each other. In this work, the type of acid sites on both zeolite Y and alumina could be tailored using H₃BO₃ and NH₄BF₄ as modifiers. Specially, H₃BO₃ remarkably reduced the amount of Lewis acid site of USY while slightly reduced the Brönsted acid sites.

3.4 Stability properties

The hydrothermal stability of the catalysts is one of the key factors own to the extreme operating conditions for FCC process. Fig. 11 presents the XRD results of hydrothermally treated USY zeolites at 800 °C for 4h. After hydrothermal treatment, the typical Y zeolite peaks are retained for all samples but with decreased crystallinity intensity compared to the raw USY zeolite due to framework damage. With increasing the boric acid amounts, the reduction of relative crystallinities of modified USY zeolites increased slightly. It was attributed to the partial framework dealumination or the removal of the extra-framework aluminum species in the cages or channels [18]. The stability of USY zeolite depends on both framework and non-framework aluminum species. The former protects the zeolite lattice by counteracting hydrolysis of framework bonds, and the latter, when located at the external crystal surface, couples with lattice defects and prevents solubilization of the zeolite framework which is the result of its low water-solubility.[42, 43] In the high H₃BO₃ usage, both framework and nonframework aluminum species were partly removed, which can lead to poor stability of modified USY for hydrothermal stability. It suggested that the amounts of boric acid in the modification should be limited in case of the sharp decrease of hydrothermal stability of USY zeolites. The boron modified equilibrium catalyst had better hydrothermal stability than sole modified USY. After the hydrothermal treatment, the relative crystallinities for Ecat and M-Ecat were 90.02% and 87.58% respectively, compared to raw materials, probably due to the protection of matrix such as aluminosilicate.

3.5 Cracking performance

3.5.1 Catalytic cracking of n-dodecane

Paraffin cracking is catalyzed by both Brönsted and Lewis acid sites on solid acid catalysts. The conversion of n-dodecane on USY and alumina is displayed in Tables 4. It shows that n-dodecane conversion changes in the order from high to low: X-USY >> BF-Al₂O₃ > γ -Al₂O₃ > B-Al₂O₃. Higher conversion on Y-type zeolite was expected due to their higher total acid amounts and acid density compared to that of alumina (Table 3). In addition, modified USY had better cracking performance than raw USY. The conversion increased from 75.18% for USY to more than 81.34% for modified USY, although the latter had reduced total acid amounts. Similarly, at lower conversions the modified USY had better cracking performances than raw USY (Table S1). This could be explained by that the Lewis acid sites were removed to a great extent while Brönsted acid sites were mostly reserved for modified USY compared to raw USY, which reinforced the cracking of n-dodecane. However, the conversion would decreased with continued reduction of total acid amount. For instance, 84.56% and 81.34% of conversions were observed for 5%-USY and 20%-USY, respectively. Besides acidity, the higher surface area and clearer microporous channels on modified USY also improved the accessibility of n-dodecane to the acid sites in its micropores.

In contrast, the conversion of n-dodecane on alumina was comparatively lower ($\leq 17.85\%$) compared to USY catalysts ($\geq 75.18\%$). For alumina, it seems like acid types rather than textural properties were responsible for the conversion of n-dodecane. It is reasonable that conversion on γ -Al₂O₃ was higher than that of B-Al₂O₃ since the latter had lower Lewis acid amount. In contrast, quite a few Brönsted acid sites on BF-Al₂O₃ substantially improved the conversion compared to γ -Al₂O₃, although the Lewis acid amounts on these two catalysts

were comparatively (Table 3).

It is well known that carbocations (carbonium ions and carbenium ions) are first formed on acid sites via protonation reaction and/or dehydrogenation[44, 45]. Thereafter, consecutive reactions such as the break-up of C-C bonds and hydrogen transfer reactions occur through the cracking of carbocations transition states[46, 47]. It has been widely recognized that the cracking of carbocations transition states proceeds via both classical β -scission cracking routes (i.e., bimolecular cracking mechanism and carbenium ion cracking mechanism) and the monomolecular protolytic cracking pathway (i.e., Haag-Dessau cracking mechanism and carbonium ion cracking mechanism)[45]. To explain the occurrence of two different cracking routes, Wielers et al.[48] had defined an index called cracking mechanism ratio (CMR) to quantitatively describe the relative contribution of each of the two cracking mechanisms. CMR was defined as “ $(C_1 + \sum C_2)/(i-C_4^0)$ ”, where C_1 and $\sum C_2$ were molar yield of methane and molar yields of ethane and ethene, respectively; $i-C_4^0$ is the molar yield of isobutane. A high value of this index (CMR>1) points to a relatively high contribution of the protolytic cracking route, whereas a low value ($0 < \text{CMR} < 1$) indicates that the classical β -scission route is the main cracking pathway. It must be mentioned that there are two conversion regimes for the catalytic cracking reactions: a) the kinetics regime at low conversion, which is better to distinguish activation energy as sequential reactions (secondary and tertiary) are minimized most of the time, protolytic cracking thus plays a primary role; b) the regime at high conversion, which is similar to a real case and products diffusion and reconversion play a main role in the catalyst activity and selectivity.

Table 4 shows that the CMR values for all zeolite Y samples were relatively small (≤ 0.18)

indicative of the dominant contribution of the classical β -scission cracking mechanism in n-dodecane conversion. Whereas the CMR values for alumina were comparatively large (>1.58) indicative of the prominent contribution of monomolecular protolytic cracking mechanism. To compare Y zeolite and alumina at the similar conversion, n-heptane was also used as the modeling feed to measure CMR values on Y zeolites (Table S1). The results (Table S1) shows that at lower n-heptane conversions (< 24 wt.%) the CMR values for Y zeolites were higher (in the ranges of 1.08~1.35) than that at high alkane conversions, indicating the protolytic cracking slightly surpasses the β -scission cracking. It seems probably that alkane cracking on Y zeolites are likely to be initiated through the monomolecule protolytic cracking routes and then classical β -scission cracking routes becomes a dominate route at high alkane conversions. It is noted that the CMR values for γ - Al_2O_3 and B- Al_2O_3 were much higher than that of BF- Al_2O_3 . Considering the presence of Brönsted acid site on BF- Al_2O_3 , it is therefore concluded that n-dodecane was more prone to cracking on Brönsted acid site following the classical bimolecular cracking mechanism, however, it was inclined to crack on Lewis acid site in the monomolecular protolytic cracking pathway. Similar experimental results about the effects of acid properties on product distributions were reported on by Abbot et al. [49, 50] in the catalytic cracking of paraffin on zeolite. Moreover, catalytic cracking performances of n-dodecane on Brönsted acid sites were much better than that on Lewis acid sites. Consequently, it is useful to influence the hydrocarbon cracking by tailoring the Brönsted/Lewis acid ratio of USY zeolites.

Hydrogen transfer rate is another indirect evidence that n-dodecane cracking occurred on Brönsted acid sites mainly via classical bimolecular β -scission mechanism. Alkenes, coming

from the initial cracking of n-dodecane, are prone to be saturated on acid sites through a bimolecular hydrogen transfer reactions, leading to higher alkane/alkene ratios. However, the hydrogen transfer rate is a function of multi-factors such as acid density and alkene density. More open channels, high concentration of alkenes, and high acid site density usually result in high hydrogen transfer rates. A coefficient C_{HT} has been therefore defined to quantitatively analyze the hydrogen transfer reaction[2, 7]. That is, a higher C_{HT} value corresponds to a faster hydrogen transfer rate. In Table 4, the C_{HT} values for Y-type catalysts (≥ 7.32) were far above that for alumina (≤ 0.96), which could be ascribed to the higher acid density and secondary reactions on the former. The contribution of secondary reactions to hydrogen transfer could be verified by the low C_{HT} values (≤ 0.86) at lower n-heptane conversions (Table S1). That is, high acid amounts on zeolite brought about high concentration of alkenes in the initial cracking stage, which indirectly improved the hydrogen transfer in the subsequent reactions.

In view of acid site types and their amounts (Table 3), we deduce that hydrogen transfer reactions relied on Brönsted acid site superior to Lewis acid site. For instance, the C_{HT} value for BF- Al_2O_3 (0.96) was much higher than that for γ - Al_2O_3 (0.38) and B- Al_2O_3 (0.27). Therefore, catalytic cracking of n-dodecane and hydrogen transfer reactions were easily affected by Brönsted acid sites and they were closely coupled and mutual promoted. However, it is noted that coke yield also increased with improving acid amount due to the enhanced hydrogen transfer reactions. In light of this, it is worth finding the sweet spot between cracking ability and coking by controlling the acid types and their densities on catalysts.

3.5.2 Catalytic cracking of VGO

It is well known that FCC catalysts are commonly composed of USY-type zeolite and alumina- or aluminosilicate- based matrix. As aforementioned, the acid property and textural property of USY and alumina had been tailored by boric acid modification. It is meaningful to explore the catalytic performance of modified equilibrium catalyst on heavy oil cracking in the modeling FCC reaction conditions. The results in Table 5 show that Ecat and M-Ecat provided similar vacuum gas oil conversions and coke yields. However, it is attractive to find that the yields of light hydrocarbons (C_2 - C_4 alkanes and alkenes) in VGO conversion on M-Ecat decreased significantly by 4.99 wt.% compared to Ecat. In contrast, the yield of gasoline on the former increased by 4.25 wt.% compared to the latter. It suggested that the acid density and acid strength on M-Ecat were suitable to improve the cracking of large hydrocarbon molecules in VGO, at the same time suppress the over-cracking reaction of light oils such as gasoline and diesel to light hydrocarbons. It could be explained by the hydrogen transfer reactions. Since the cracking rates of olefins are much faster than that of alkanes, the fast saturation of the intermediate olefins during the cracking of VGO on M-Ecat inhibited the over-cracking to some extent. It was consistent with the higher C_{HT} value of M-Ecat than that of Ecat by 45.36%. On the other hand, the coke yields of two catalysts varied little. Consequently, both USY-type zeolite and alumina-based matrix of the equilibrium catalyst were modified by boric acid, and the combined action of tailored acid and textural properties of M-Ecat contributed to the improved performances in heavy oil cracking.

4. Conclusions

The USY and equilibrium catalyst with reduced Lewis acid sites and increased Brönsted/Lewis acid ratios have been prepared using H_3BO_3 as a modifier at a mild

experimental condition. These modified USY have better performance in n-dodecane cracking and modified equilibrium catalyst has better performance in vacuum gas oil cracking, which is mainly ascribed to the tailored acid sites. A comparison with modified alumina catalysts shows that Brönsted acid site has a more positive effect on the catalytic activity than Lewis acid site. However, Brönsted acid site at high concentration accelerates the hydrogen transfer reactions which brings about high coke yield. So, it is worth finding the sweet spot between cracking ability and coking by controlling the acid types and their densities on catalysts. In the VGO cracking on equilibrium catalysts, the over-cracking of gasoline and coking formation reactions were well inhibited simultaneously.

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Tables

Table 1 Properties of VGO feedstock and Ecat

VGO properties		Ecat properties	
Density (20 °C), kg/m ³	915	Molecular sieve type	USY
Hydrogen, wt%	12.41	Al ₂ O ₃ , wt%	48.2
Sulfur, wt%	3.07	Abrasion index, %	2.1
Conradson carbon, wt%	0.48	Bulk density, kg/m ³	730
Nitrogen, wt%	<0.1	Size distribution (ψ), %	
Saturates, wt%	58.88	0-40 μm	12.0
Aromatics, wt%	35.29	0-149 μm	95.6
Colloid, wt%	5.83	Mean grain size (d), μm	76
Ni, μg/g	33	Ni, μg/g	4410
V, μg/g	115	V, μg/g	1520

Table 2. Textural and composition properties of H₃BO₃ modified samples

items	S _{BET} (m ² /g)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	a ₀ (Å)	SiO ₂ /Al ₂ O ₃	B content (wt.%)
USY	583	505 ^a	0.382	0.255 ^b	24.4846	9.35 ^c (5.91) ^d	0.00 (0.00) ^e
2%-USY	620	538	0.433	0.279	24.4348	11.70 (6.45)	0.71 (0.68)
5%-USY	615	538	0.396	0.279	24.4125	13.05 (7.70)	1.68 (1.76)
10%-USY	610	533	0.392	0.275	24.3887	14.86 (8.55)	3.04 (3.21)
20%-USY	602	527	0.389	0.271	24.3510	18.80(10.47)	3.57 (3.76)
Ecat	144	92	0.193	-	-	-	0.00
M-Ecat	155	95	0.194	-	-	-	1.05
γ-Al ₂ O ₃	303	-	0.678	-	-	-	0.00
B-Al ₂ O ₃	344	-	0.666	-	-	-	0.25
BF-Al ₂ O ₃	241	-	0.626	-	-	-	0.29

^a micropore surface area obtained by t-plot method; ^b micropore volume obtained by t-plot method; ^c framework SiO₂/Al₂O₃ molar ratio derived from XRD analysis; ^d SiO₂/Al₂O₃ molar ratio derived from XRF analysis; ^e boron content detected by ICP-AES method and XPS in the brackets.

Table 3. Acidity properties of Ecat, USY, and γ -Al₂O₃ before and after modification

Item	Total acidity ($\mu\text{mol}\cdot\text{g}^{-1}$)	BAS ($\mu\text{mol}\cdot\text{g}^{-1}$)	LAS ($\mu\text{mol}\cdot\text{g}^{-1}$)	BAS/LAS ratio
USY	293.35	114.71	178.64	0.64
2%-USY	257.68	139.23	118.45	1.18
5%-USY	205.80	117.01	88.79	1.32
10%-USY	168.67	102.50	66.17	1.55
20%-USY	135.52	82.65	52.87	1.56
Ecat	32.64	11.55	21.09	0.55
M-Ecat	23.94	12.91	11.03	1.17
γ -Al ₂ O ₃	19.62	0.00	19.62	0.00
B-Al ₂ O ₃	6.20	0.00	6.20	0.00
BF-Al ₂ O ₃	8.83	2.96	5.87	0.50

Table 4 Catalytic cracking performances of n-dodecane on modified USY and alumina

Item	USY	2%-USY	5%-USY	10%-USY	20%-USY	γ -Al ₂ O ₃	B- Al ₂ O ₃	BF- Al ₂ O ₃
Yield (wt%)								
H ₂	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01
Dry gas	0.88	1.00	1.04	1.30	1.23	2.07	1.15	1.69
C ₃ ⁼ + C ₄ ⁼	1.81	1.30	1.35	1.57	1.71	5.14	3.16	7.66
LPG	25.10	27.71	28.95	35.85	34.51	7.09	4.01	15.02
Liquid yield ^a	67.50	63.25	60.86	55.14	57.39	89.96	94.72	82.85
Coke	6.51	8.03	9.13	7.68	6.85	0.24	0.11	0.43
Conversion ^b	75.18	84.04	84.56	84.10	81.34	9.43	5.28	17.85
C _{HT} ^c	7.32	11.60	11.43	12.38	10.54	0.38	0.27	0.96
CMR ^d	0.17	0.18	0.18	0.18	0.18	9.27	9.06	1.58

^a Collected liquid in which C₅⁺ was more than 99 wt% after reaction; ^b Converted n-dodecane; ^c C_{HT} was defined and calculated by $C_{HT} = (C_3^0 + C_4^0) / (C_3^= + C_4^=)$; ^d CMR was defined as $((C_1 + \sum C_2) / (i-C_4^0))$.

Table 5 Catalytic cracking performances of VGO on Ecat and M-Ecat catalysts

Item	Ecat	M-Ecat	Difference
Product yield (wt%)			
H ₂	0.15	0.07	- 0.08
Dry Gas	2.08	1.28	- 0.80
Ethylene	0.84	0.52	- 0.32
Propylene	5.00	2.85	- 2.15
LPG	16.40	12.21	- 4.19
Gasoline	41.47	45.72	+ 4.25
Diesel	24.01	25.11	+ 1.10
Slurry	7.41	7.15	- 0.26
Coke	5.79	5.67	-0.12
Light oil yield ^a	65.48	70.83	+ 5.35
Total liquid yield ^b	81.88	83.04	+ 1.16
Conversion ^c	89.90	90.06	+ 0.16
C _{HT}	0.97	1.41	+ 0.44

^a Sum of gasoline and diesel; ^b Sum of LPG, gasoline and diesel; ^c Sum of product yields except slurry.

Figure captions

Fig. 1. X-ray diffraction patterns of (a) modified USY and (b) its sectional magnification.

Fig. 2. X-ray diffraction patterns of alumina samples (a) and equilibrium catalysts (b). The inset of (b) is the magnification of (331) lattice plane.

Fig. 3. ^{27}Al MAS NMR spectra of modified USY.

Fig. 4. ^{29}Si MAS NMR spectra of H_3BO_3 modified USY.

Fig. 5. (a) Contents of framework Al(IV) and non-framework Al(VI) on the Al_2O_3 basis, derived from ^{27}Al NMR spectra; (b) framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios derived from ^{29}Si NMR spectra and XRD analysis.

Fig. 6. (a) N_2 sorption isotherms and (b) the pore size distributions of USY.

Fig. 7. Difference spectra of X-USY: (a) pyridine absorbed on acid sites and (b) OH stretching vibration region, measured at 25 °C after outgassing of pyridine at 150°C.

Fig. 8. (a) Acid amount and (b) Brönsted/Lewis acid ratio of modified USY at various H_3BO_3 usage.

Fig. 9. XPS spectra of the H_3BO_3 modified USY. (i) Al_{2p} ; (ii) B_{1s} ; (a) USY, (b) 2%-USY, (c) 5%-USY, (d) 10%-USY, (e) 20%-USY.

Fig. 10. Difference spectra of modified $\gamma\text{-Al}_2\text{O}_3$ with pyridine absorbed on acid sites, measured at 25 °C after outgassing of pyridine at 150°C.

Fig. 11. (a) XRD patterns of USY zeolites after hydrothermal treatment at 800 °C for 4 h and (b) their crystallinity reduction after hydrothermal treatment compared with raw USY.

Figures

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Fig. 10. Difference spectra of modified $\gamma\text{-Al}_2\text{O}_3$ with pyridine absorbed on acid sites, measured at 25 °C after outgassing of pyridine at 150 °C.

Fig. 11. (a) XRD patterns of USY zeolites after hydrothermal treatment at 800 °C for 4 h and (b) their crystallinity reduction after hydrothermal treatment compared with raw USY.

Graphical Abstract