

The application of mesoporous alumina with rich Brönsted acidic sites in FCC catalysts

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Abstract To decrease the coke yield while increase the conversion of FCC feedstock is of great significance as the crude oil becoming heavier and poorer in quality. In this work, the modified mesoporous alumina with rich Brönsted acidic sites (BAS) and reduced Lewis acidic sites (LAS) have been prepared by a sol-gel method. The modified γ -Al₂O₃ was characterized by X-ray diffraction, N₂ sorption and FT-IR analysis and then used as the binder in FCC catalyst for catalytic activity tests. The results showed that the modified γ -Al₂O₃ (M-2) possessed a high BAS/LAS pyridine-IR band ratio of 0.75. The new catalysts with modified γ -Al₂O₃ (New-2) showed a good performance in increasing conversion of FCC feedstock by 8.55 % but reduced the coke yield by 3.25 % compared with catalyst of commercial alumina sol binder (C-AS). Besides, the New-2 increased the gasoline yield and diesel yield by 7.02 and 3.02 %.

Keywords Brönsted acidic sites · Mesoporous alumina · Coke formation · FCC

Introduction

Fluid catalytic cracking (FCC) is one of the most important conversion technologies to produce transportation fuels and petrochemicals. It has been widely adopted to transform high-boiling, high-molecular weight petroleum hydrocarbons into valuable distillates such as olefins, gasoline, and diesel in the last decades. Modern FCC catalysts consist of two main components: (1) zeolites which provide the main active sites for the oil conversion and gasoline fraction, and (2) the matrix which offer the physical characteristics of the catalysts and extra acidic sites for pre-cracking heavier fractions [1, 2]. γ -Al₂O₃ has been extensively used as one of the most important binder as well as the matrix materials in FCC catalysts due to its good adhesive properties, physical performances, and acidity for pre-cracking of hydrocarbon macromolecules [3]. However, traditional γ -Al₂O₃ possesses only Lewis acidity which causes excessive hydrogen transfer reactions and results in severe coke formation [2, 4]. So an innovative idea is to reduce Lewis acidity and/or generate more Brönsted acidic sites which are more conducive to cracking by surface modification of γ -Al₂O₃ in order to reduce the coke formation.

Hetero atoms such as silicon and phosphorus were commonly added to the surface alumina to adjust the acidity of γ -Al₂O₃ [5, 6]. Fluorine modified γ -Al₂O₃ was found to have low content of Brönsted acidic sites and fluorine modification has been widely studied [7–10]. Rodriguez and Moreno [8, 9] prepared partially fluorinated alumina catalysts by incipient wetness impregnation with NH₄F and observed that active Brönsted sites were formed by doping lower fluorine content. Dambournet and Zheng [11, 12] also observed the occurrence of weak Brönsted acid sites and suggested that the acid sites were associated with the dissociation of surface water

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molecules by the strongly under-coordinated species. In other research, no Brönsted acid sites have been observed on fluorine modified alumina [10, 13, 14]. Besides, the amount of Lewis acid sites increased with fluorine content at lower F doping amount which is unfavorable to be used as FCC catalyst components [3, 15, 16]. In contrast, it was reported that the introduction of boron into γ -Al₂O₃ increased its surface area as well as the concentrations of acid sites [15, 17]. However, the acid type was not mentioned and the acid sites were thermal instable. Whereas, few reports about alumina modification by NH₄BF₄ have been published. Therefore, it is interesting to synthesize γ -Al₂O₃ with improved Brönsted acid sites and to characterize these materials for their application as a matrix in FCC catalysts.

With this aim, a sol-gel method was adopted to modify the surface acidity of γ -Al₂O₃ using NH₄BF₄ as modifier. The modified γ -Al₂O₃ was then characterized by XRD, N₂ sorption and FT-IR to investigate the crystalline structures, porosity and the surface acidity. The catalytic activities of FCC catalysts were also tested using the modified γ -Al₂O₃ as the binder.

Experimental section

Preparation

Pseudo-boehmite (Al₂O₃ content is 71.90 wt% on a dry basis), Kaolin clays and zeolite USY were purchased from Hua Xin powder Co. Ltd. Ammonium hydroxide (28.00 wt%) and nitric acid (HNO₃, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ammonium fluoroborate (NH₄BF₄ 97.00 wt%) was purchased from Shanghai SSS Reagent Co. Ltd.

The modified γ -Al₂O₃ was prepared by a modified sol-gel route [18]. The samples were prepared as follows. Pseudo-boehmite was dispersed in 40 ml of distilled water and then 35 ml of NH₄BF₄ aqueous solution was added at 85 °C under vigorous stirring. Nitric acid was added into the solution until pH = 3. The whole suspension was then stirred vigorously for 6 h. Thereafter, aqueous ammonia was added into the solution to adjust to a pH of 11. The quiescent suspension was aged at 75 °C for 24 h. The resulting gel was subsequently washed with distilled water and dried at 85 °C for 24 h. The sample was finally obtained by heating the dried material under air at 550 °C for 4 h. Two modified γ -Al₂O₃ samples, marked as M-1 and M-2, were prepared at selected F/Al atomic ratios of 0.20, 0.40.

Four types of binders, commercial alumina sol, commercial silica sol, M-1 and M-2, were selected to compare their catalytic activity. The catalysts, named them in turn

C-AS, C-SS, New-1 and New-2, were prepared with the USY, kaolin and binder at a dry basis mass ratio of 30:40:30. All catalysts were hydrothermally treated in 100 % water steam at 800 °C for 4 h before catalytic activity tests.

Characterization

XRD patterns were recorded on a Bruker Axs diffractometer (Germany) using Cu-K α radiation generated at 40 kV and 40 mA. A scanning range from 5° to 75° was used at a speed of 0.01°/s. N₂ isothermal sorption measurements at -196 °C were carried out in a Micrometrics TRISTAR 3000 analyzer. The samples were first outgassed at 300 °C with a vacuum degree of 10⁻² torr for 4 h prior to N₂ sorption measurement. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using experimental points at a relative pressure (P/P₀) = 0.05–0.25 and total pore volume using a single point adsorption at (P/P₀) = 0.99. The pore size distribution was derived from the desorption branch, using the Barrett–Joyner–Halenda (BJH) method [19]. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer equipped with a MCT liquid nitrogen cooled detector and a KBr beam splitter. The spectra of the samples were recorded by accumulating 64 scans at 4 cm⁻¹ resolution [20]. The transmission electron microscopy (TEM) images were acquired on a JEOL JEM 2100 electron microscope operated at an accelerating voltage of 200 kV.

Catalytic evaluation

Catalytic activity tests of catalysts were performed in an automated bench-scale micro-activity test (MAT) unit. The catalytic reactions occurred at 500 °C for 75 s, using 3.00 g of catalyst in a tubular stainless steel reactor with inner diameter of 13 mm and length of 180 mm and 1.00 g feed. Vacuum gas oil (VGO) as heavy hydrocarbon feedstock. VGO was purchased from Fushun Petrochemical Co. (Table 1 as provided by vendor). The resulting cracking gas was collected and analyzed by a Varian 3800 gas chromatograph (GC) equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). The liquid products were weighed and analyzed by simulated distillation on a Varian 3800 GC according to the ASTM D2887 method. So, the mass percentage of gasoline (IBP–204 °C), diesel (204–350 °C), and slurry (>350 °C) were quantified. The Elemental Analyzer (Elementar Vario EL III) was used for measuring the weight of coke deposited on the catalyst by analyzing the CO₂ and CO quantities after combustion.

Table 1 Feedstock properties of second vacuum side-streams of Fushun Refinery

Items		Items	
Density (20 °C) (kg/m ³)	858.4	Metal content (wt%)	
Conradson carbon (wt%)	0.11	V	0.01
Element composition (wt%)		Ca	0.44
C	85.52	Fe	6.16
H	13.86	Ni	0.05
S	0.09	Group composition (wt%)	
N	0.16	Saturates	89.48
Boiling range (°C)		Aromatics	8.38
HK	385.2	Colloid	2.14
50 %	465.7	Asphaltenes	0
KK	479.6		

Results and discussion

The XRD patterns in Fig. 1 showed that the pseudo-boehmite raw material had two crystalline phases of boehmite and bayerite. It was transformed into the γ -Al₂O₃ phase after a simple heating at high temperature via dehydroxylation and reconstruction reactions. Similarly, the NH₄BF₄ modified alumina, M-1 and M-2, possessed only γ -Al₂O₃ crystalline phases. However, the elemental analysis demonstrated that the fluorine contents on them were above 4 % (not shown here). It indicated that the modification process did not change the long range order composition of γ -Al₂O₃ phase.

The further investigation of textural properties of samples, however, showed that after modification, M-1 and M-2 had lower specific surface areas but increased pore volumes compared with γ -Al₂O₃ (Table 2). Simultaneously, the pore width of modified alumina increased from 5.7 nm to about

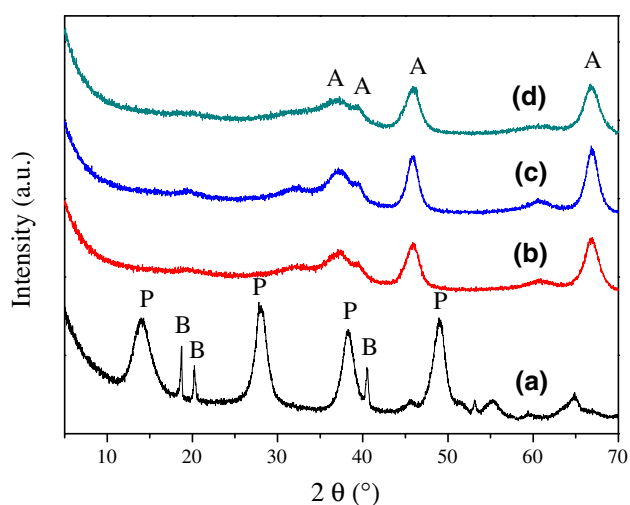


Fig. 1 XRD patterns of samples: *a* pseudo-boehmite, *b* γ -Al₂O₃, *c* M-1 and *d* M-2. (*P* boehmite, *B* bayerite, *A* γ -Al₂O₃)

7.0 nm. It is probably because that γ -Al₂O₃ partially reacted with fluorine to form the hydroxyl fluoride phase although it was undetected by XRD analysis, however, this framework was of a dense packed stacking and lower surface area [13]. The TEM images of M-2 showed that the modified alumina was the aggregation of nanostructure particles with sizes ca. 20 nm and M-2 showed an open channel structures (Fig. 2).

The acidities of alumina before and after modification were determined by pyridine FT-IR spectra (Fig. 3). The band at 1490 cm⁻¹ was generally ascribed to the combined Brønsted and Lewis acidic sites. In pyridine IR spectra of all additives, there were four bands for γ -Al₂O₃ at about 1,444, 1,577, 1,593 and 1,614 cm⁻¹ which could be attributed to the Lewis acidic sites [20]. After modification, another three bands at 1,543 and 1,643 cm⁻¹ appeared for M-1 and M-2. It was attributed to Brønsted acidic sites. In addition, the associated shoulder band at 1,453 and 1,597 cm⁻¹ was assigned to strong Lewis acidic sites [21, 22]. Therefore, the modification of γ -Al₂O₃ using NH₄BF₄ led to the creation of Brønsted acidic sites.

The band areas of Brønsted acidic sites and Lewis acidic sites were calculated to compare the changes of acid amounts because of the unknown absorption coefficient (Table 2). It was obvious that the total acidity amount decreased by ca. 18.77 % for both modified alumina. In contrast, the Lewis acidity, respectively, decreased by 47.45 and 53.73 % for M-1 and M-2 while the generated Brønsted acidic sites were, respectively, up to 1.897 and 2.308. The more modifier was used, the higher BAS and lower LAS were obtained in our experimental conditions. M-2 had a high BAS/LAS pyridine-adsorbed band ratio up to 0.75.

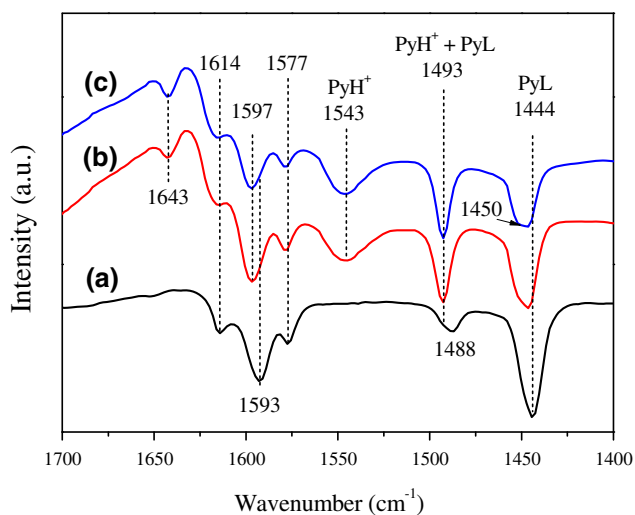
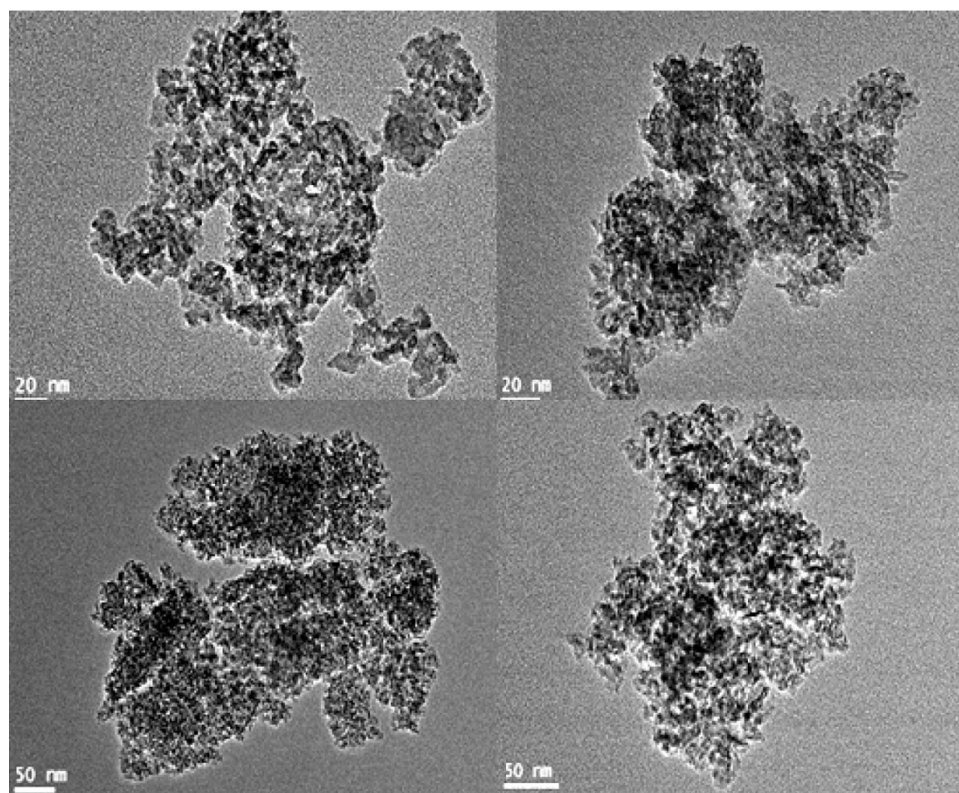
It is universally recognized that both Brønsted and Lewis acidic sites on FCC catalysts can initiate the hydrocarbon reactions by forming carbonium/carbenium ions [23, 24]. It involves C–C bond breakup in parallel-series reactions via β -scission and hydrogen transfer, which convert high molecule hydrocarbons into light distillates, gases and coke [25]. In particular, LAS can give rise to much higher coke formation since their reactions are initiated by dehydrogenation or hydrogen transfer reactions of hydrocarbons [2, 4]. In this work, four FCC catalysts have been prepared to examine the effects of acidity on cracking abilities and coke formation, using four types of binders of the conventional alumina sol which had the LAS alone, silica sol with low acidity, modified alumina M-1 and M-2 with the varied BAS and LAS.

The results in Table 3 showed that C-AS, C-SS, New-1 and New-2 had the orderly increased conversions and light oil yields, indicating their increased cracking abilities of hydrocarbons. The similar trends occurred on the yields of gasoline and diesel. On contrary, the yields of dry gas and coke decreased orderly for them.

Table 2 Textural properties and acidity of FCC catalyst and additives

Items	S _{BET} (m ² /g)	V (cm ³ /g)	Pore width, (nm)	BAS area (~1,540 cm ⁻¹)	LAS area (~1,450 cm ⁻¹)	Total area
γ-Al ₂ O ₃	237	0.35	5.7	0	6.616	6.616
M-1	234	0.41	7.0	1.897 ^a	3.477	5.374
M-2	231	0.41	7.1	2.308	3.061	5.369

^a The area was calculated from the correction absorbance band and it had no quantitative unit

Fig. 2 The TEM images of modified alumina (M-2)**Fig. 3** FT-IR spectra of pyridine adsorbed samples: *a* γ-Al₂O₃, *b* M-1 and *c* M-2**Table 3** Catalytic performance of different catalysts for cracking

Items	C-AS	C-SS	New-1	New-2
Yield (wt%)				
H ₂	0.04	0.06	0.05	0.06
Dry gas	1.00	0.95	0.66	0.59
Olefin	6.38	5.70	5.47	6.14
LPG	9.38	10.88	13.98	11.25
Gasoline	39.29	40.76	45.22	46.31
Diesel	15.65	16.11	18.02	18.67
Slurry	26.69	24.65	18.85	18.14
Coke	3.84	2.65	0.70	0.59
Conversion	73.31	75.35	81.15	81.86
Light oil yield	54.94 ^a	56.87	63.24	64.98
Total liquid yield	64.32 ^b	67.75	77.22	76.23
Loss	4.11	3.94	2.52	4.39

^a Light oil yield was the sum of gasoline and diesel

^b Total liquid yields were the sum of LPG, gasoline and diesel

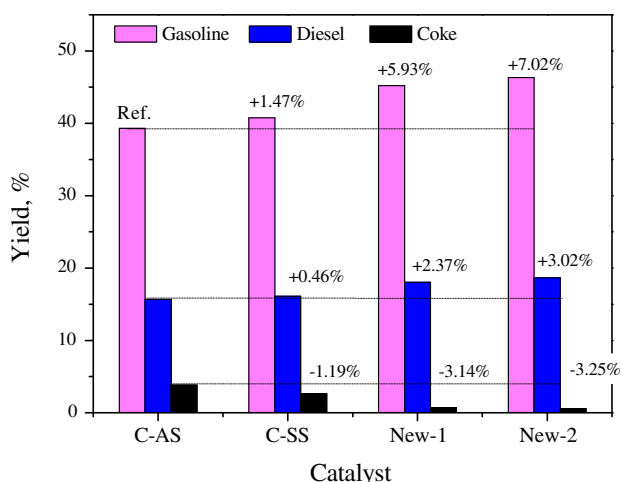


Fig. 4 The differences of the yields of gasoline, diesel and coke using the catalysts taken C-AS as a reference

The advantages of the introduction of Brønsted acidic sites were better illustrated by the comparison of the yields of gasoline, diesel and coke taken C-AS as a reference (Fig. 4). The results demonstrated that New-2 had the best performance in improving the gasoline yield by 7.02 % and diesel yield by 3.02 %, simultaneously, decreasing the coke formation by 3.25 %. The better performances of New-2 catalyst than New-1 catalyst coincided with the results of the increased BAS and reduced LAS of M-2 compared with M-1 in Table 2. The lower coke yield of C-SS was probably ascribed to its lower acidic sites compared with C-AS since it is known that matrix derived from silica sol by heating has very few acidic sites. Therefore, it was reasonable to draw the conclusion that the Lewis acidic sites were responsible for the coke formation while Brønsted acidic sites were favourable to the decrease of coke formation. On the other hand, the combined effects of Brønsted and Lewis acidic sites increased the conversion of hydrocarbons to produce more gasoline and diesel.

Conclusion

By the modification of alumina with NH_4BF_4 , the alumina with rich Brønsted acidic sites and reduced Lewis acidic sites were prepared. The modified alumina showed pure $\gamma\text{-Al}_2\text{O}_3$ crystalline phase and without obvious changes of pore structures. As the binder in FCC catalysts, the new catalysts with modified $\gamma\text{-Al}_2\text{O}_3$ had a good performance in hydrocarbon conversion which remarkably reduced the coke formation and increased the yields of gasoline and diesel.

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