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Maximizing Gasoline Yield in Catalytic Cracking of VGO through Post-synthesis Modification of USY Zeolite

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Abstract

USY zeolite as a crucial component in FCC catalyst has been modified via post-synthesis acid treatment applying acetic acid, oxalic acid, and hydrochloric acid in order to increase mesoporosity and more pore accessibility. Acid leaching was performed under two different conditions including room temperature and reflux. Extra-framework Al atoms were removed which was confirmed through XRD, SEM, ICP-OES and N2 adsorption-desorption isotherm analyses. Elemental analysis showed increasing in SiO_2 to Al_2O_3 ratio. Examining surface area and pore volume through BET-BJH and t-plot methods showed that total surface area, as well as mesoporous volume, were increased by acid-treating in all modified zeolites. The mesoporous surface was increased from 52.62 in primary zeolite to 115.09 m^2/g in the sample which was acid leached through oxalic acid at room temperature. Moreover, the total surface area of the zeolite was increased from 684 to 743 m^2/g. All modified zeolites were applied in the preparation of FCC catalyst. Catalytic cracking of VGO indicated a considerable increase in gasoline yield upon modified catalysts. Gasoline yield was increased from 18 wt.% over FCC to 40 wt.% in acetic acid-modified zeolite at room temperature.

Keywords: USY zeolite, Post-synthesis Modification, FCC Catalyst, Catalytic Cracking, Gasoline.

INTRODUCTION

Zeolites are important groups of porous materials which have broad applications in a wide variety of catalytic applications [1]. Zeolite Y is a crystalline aluminosilicate material widely used in petrochemical industries. One of the most important applications of zeolite Y is in fluid catalytic cracking (FCC) process. FCC is of crucial technologies to the conversion of heavy petroleum products such as fuel oil, vacuum gas oil (VGO) and atmospheric residues to more valuable products including gasoline, diesel and light olefins [2]. According to the increasing rate of gasoline consumption in the world, the approaches of increasing gasoline yield produced through the FCC process attract more attention.

The main problem in applying zeolites in the FCC process is the low-speed distribution and transfer of feedstock and products through small pores of the zeolites [3]. In order to overcome this problem, several approaches are presented for modification of zeolite structures. Acid leaching as a facile and economic process has attracted more attention to modify the structure of the zeolite [4].

In the present study, three acids including oxalic acid, acetic acid, and hydrochloric acid were applied for acid leaching of ultrastable Y zeolite (USY). Acid leaching was performed under two different conditions including room temperature and reflux. Extra-framework Al atoms were got-out which was confirmed through XRD, SEM, ICP-OES, and N_2 adsorption-desorption isotherm analyses. All zeolites were applied in the preparation of FCC catalyst. The performance of the prepared FCC catalysts was investigated in catalytic cracking of VGO to investigate the products distribution. Catalytic cracking of VGO indicates a considerable increase in gasoline yield upon modified catalysts. Gasoline yield was increased from 18 wt.% over FCC to 40 wt.% in acetic acid-modified zeolite at room temperature.

METHODOLOGY

USY zeolite and kaolin were prepared from JIULONG and SAMCHUN Companies. Other materials were purchased from Merck and used without additional purification.

The X-ray diffraction (XRD) patterns of the catalysts were recorded on Philips X’Pert MPD diffractometer using Cu Kα radiation (λ = 1.54056 Ǻ) at 40 kV and 30 mA. The morphology and size of the prepared FCC catalyst were determined using a VEGA/TESCAN scanning electron microscopy (SEM). TEM measurement was obtained on a Philips CM10 transmission electron microscope using an acceleration voltage of 100 kV. Adsorption/desorption isotherms were investigated through N_2 physisorption measurements at 77 K on a Belsorp-mini II sorption analyzer. Pore volume was estimated according to the Barret-Joyner-Halanda (BJH) method. Elemental analysis of prepared FCC catalysts was determined by Genesis ICP-OES. Gas chromatographic analysis of the products from catalytic tests was performed using Agilent technology 7890A fast RGA GC instrument equipped with FID and TCD detectors for the quantitative determination of light hydrocarbons up to C4. The mass of the catalyst was 4.0 g. 1.0 to 1.5 g VGO was injected on the catalyst bed with nitrogen as inert carrier gas. The liquid products (C5+) were collected in an ice bath at the downstream and were characterizes and separated through distillation method.

H-USY ZEOLITE PREPARATION

As Na in USY zeolite causes a reduction in activity and stability of zeolite, the H-form of the zeolite is needed to apply in catalytic tests. This process was done via ion exchange of ammonium nitrate salt [5].10 g of zeolite was added to 100 mL 0.5 M ammonium solution and were stirred for 2 h in 70 ˚C. After filtration and washing with 100 mL water, the solid was dried at 120 ˚C for 12 h. Finally, the calcinations was done at 650 ˚C.

ACID LEACHING

Acid solutions of 0.1 N concentration including oxalic acid, acetic acid, and hydrochloric acid were prepared separately. 3 g of H-USY zeolite prepared in the previous section was added to 30 mL of each acid solution. The reaction mixtures were stirred under two different conditions including room temperature and reflux condition for 24 and 5 h, respectively. After that, filtration and washing following by drying and calcinations were done.

FCC CATALYST PREPARATION

In order to prepare the FCC catalysts, the primary USY zeolite, as well as all modified zeolites, were separately mixed with alumina, kaolin, and alumina-silica sol in 30wt% of zeolite. The slurries were mixed for 24 h and introduced to the spray drying instrument. The prepared catalysts were evaluated in catalytic cracking reaction. For cracking tests, 4 g of each catalyst was applied.

CATALYTIC TEST

Catalysts assessment was done in a fixed-bed reactor. The set-up was composed of a cylindrical quartz reactor, electrical furnace, and an injection system including a syringe and injection pump. The schematic diagram of the set-up is presented in figure 1. All catalytic tests were done at 550 ˚C. The purpose of catalytic tests was to investigate and comparison of the modified zeolites in catalytic cracking of VGO and the products distribution. The catalysts were named as HCl-HUS-1, HCl-HUS-2, AC-HUS-1, AC-HUS-2, OX-HUS-1 and OX-HUS-2 which starts with the acid used and the code numbers 1 and 2 relate to the samples prepared at room temperature and reflux condition, respectively.

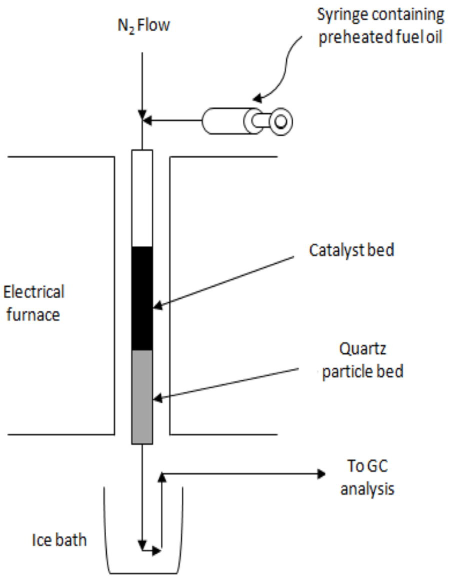

Figure 1: Schematic of catalytic cracking set-up

DISCUSSION AND RESULTS

XRD patterns of the samples showed that the crystalline framework of the zeolites was unchanged after acid leaching with all three acids. Calculating the crystallinity value of the zeolites indicated that conversion of Na-USY to H-USY, increased the crystallinity from 90 to 93% and this value was further increased to 96% for acid-treated samples at reflux condition (AC-HUS-2), OX-HUS-2 and (HCl-HUS-2). However, despite increasing the crystallinity value under reflux condition, this value was decreased for samples treated at room temperature. This observation could be assigned to the more reaction time in room temperature condition in which more contact time of zeolite with acid caused partially deformation of the zeolite framework.

Elemental analysis confirmed the Na reduction in H-USY zeolite. The corresponded values are reported in Table 1. It is clear from the table that acid modification of the zeolites led to increasing of SiO_2/Al_2O_3 ratio. This result is again a confirmation of exiting extra-framework Al atoms from the pores without changes in Al atoms in the zeolite framework; due to XRD results.

Comparison of SEM image of the primary zeolite with all treated samples shows that the morphology of samples doesn't affect by the acid leaching process. For more clarification, the SEM images of two samples including H-USY and OX-HUS-1 is shown in Figure 2a and 2b, respectively. TEM image of OX-HUS-1 zeolite confirms the existence of mesopores in the modified zeolite structure (Figure 2c).

Table 1: Elemental analysis of zeolites before and after acid leaching.

Sample	SiO_2 (Wt.%)	Al_2O_3 (Wt.%))	SiO_2/Al_2O_3	Na_2O (Wt.%))
Na-USY	62.77	20.27	3.09	1.68
H-USY	68.71	20.85	3.27	0.28
HCl-HUS-1	68.98	20.65	3.34	0.18
HCl-HUS-2	69.21	20.32	3.40	0.16
AC-HUS-1	71.14	20.89	3.40	0.13
AC-HUS-2	71.61	20.47	3.49	0.11
OX-HUS-1	71.65	19.29	3.71	0.16
OX-HUS-2	72.27	18.66	3.87	0.17

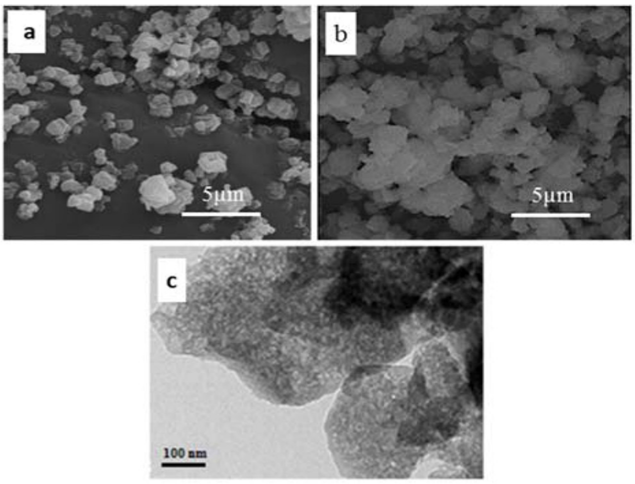

Figure 2: SEM images of H-USY (a), OX-HUS-1 (b) and TEM image of OX-HUS-1 (c) samples.

Physicochemical characteristics of the zeolites were listed in Table 2. From the table, it is clear that the surface area is increased for all treated zeolite compared to the primary zeolite (684 m^2/g) and the maximum surface area of 743 m^2/g was observed for OX-HUS-1 sample. T-plot shows that the mesoporous volume was increased in acid-treated samples compared to H-USY zeolite (0.139 ml/g). The maximum mesoporous volume of 0.188 mL/g was observed for OX-HUS-1. This sample had also the maximum pore volume (0.326 mL/g) and surface area. The results in Table 2 clearly show this claims. These observations highlighted the reasonable performance of oxalic acid in acid leaching of USY zeolite. BJH plot demonstrates the increase in pore sizes in modified zeolites regards to the H-USY zeolite. The pore size of 1.8 nm in H-USY zeolite is enhanced to 4-10 nm, in which the highest pore size value of 10 nm is related to OX-HUS-1 sample.

Catalytic tests were performed with the FCC catalysts which are prepared from modified zeolites as well as the H-USY zeolite. The results containing the products yield obtained over different catalysts are listed in Table 3. The catalysts were names as FCC-HCl-1, FCC-HCl-2, FCC-AC-1, FCC-AC-2, FCC-OX-1 and FCC-OX-2 in which the name of acid used for leaching process comes after FCC phrase and the numbers 1 and 2 relates to the reaction medium of room temperature and reflux conditions, respectively.

Table 2: Physicochemical properties of USY zeolite before and after acid leaching.

Sample	Meso volume (mL/g)	Micro volume (mL/g)	Surface area (m^2/g)	Pore volume (mL/g)	Meso surface (m^2/g)
H-USY	0.139	0.18	684	0.318	52.62
HCl-HUS-1	0.158	0.164	700	0.322	94.79
HCl-HUS-2	0.150	0.171	698	0.321	91.85
AC-HUS-1	0.165	0.160	703	0.325	123.28
AC-HUS-2	0.159	0.163	700	0.322	95.61
OX-HUS-1	0.188	0.138	743	0.326	187.09
OX-HUS-2	0.180	0.139	741	0.319	158.58

Table 3: Product distribution of cracking catalyst over VGO.

Yield (wt.%)							
	FCC	FCC-HCl-1	FCC-HCl-2	FCC-OX-1	FCC-OX-2	FCC-AC-1	FCC-AC-2
Ethylene	4.9	3.75	4.23	2.80	3.62	3.73	23.4
Propylene	11.90	10.38	9.98	11.20	9.24	8.98	10.79
Butenes	2.97	3.01	2.58	3.81	2.93	2.41	173
Alkanes	32.48	28.7	30.42	19.37	28.94	28.21	34.5
Dry gas	3.26	2.32	2.87	1.33	2.67	2.19	2.86
Gasoline	18	29	27	40	32	29	24

The data in Table shows that the gasoline yield in cracking reaction was increased overall modified zeolites. Among three acids applied, the highest gasoline yield of 40wt% was obtained over FCC-OX-1 catalyst which was prepared by USY zeolite modified by oxalic acid at room temperature. The second order of gasoline yield of 32 wt% belongs to FCC-OX-2 catalyst which was prepared by USY zeolite modified by oxalic acid at reflux conditions. These values compared to the gasoline yield of 18 wt% obtained over the catalyst prepared from the primary H-USY zeolite are perfectly significant.

On the other hand, these results are in good accordance with the physicochemical characteristics of the zeolites which were discussed former. The catalyst prepared from the zeolite with a maximum surface area and the maximum mesoporous volume showed the best performance in catalytic cracking in terms of enhancing the gasoline yield. Moreover, a comparison of gasoline yield among the modified catalysts proved that the catalysts prepared from the zeolites modified at room temperature resulted in more gasoline yield in cracking experiment rather than the catalyst prepared from the zeolites modified under reflux condition. The modified catalyst also produced less dry gas (Methane and hydrogen) than the primary zeolite; in a way, that dry gas yield was decreased from 3.26 wt% in unmodified FCC catalyst to 1.33 wt% in FCC-OX-1.

It is noticeable that despite the significant increase in gasoline yields over modified catalysts in the present work, other cracking products including light olefins and alkanes experienced low reduction (Table 3). This raises the importance of this work achievement.

CONCLUSIONS

In the present study, USY zeolite as a crucial component of FCC catalyst was modified via acid leaching through the post-modification method. Acid leaching was performed via three acids including oxalic acid, acetic acid and hydrochloric acid under two different conditions comprising room temperature and reflux. The results showed that extra-framework Al atoms were getting out from the zeolite pores without destroying the crystalline framework as well as the zeolite morphology. This process resulted in zeolites with higher SiO2/Al2O3 ratio. Modification of USY zeolite resulted in enhancing the mesoporous volume of the zeolite by decreasing the microporous volume.

The modified zeolites were applied in FCC catalyst preparation. Investigation of the performance of catalysts in catalytic cracking of VGO showed the zeolite modification though acid leaching caused a significant increase in gasoline yield and reduction of dry gas production. The maximum gasoline yield was obtained over FCC-OX-1 which was prepared via the USY zeolite modified by oxalic acid at room temperature. Gasoline yield was increased from 18 wt% over FCC catalyst to 40 wt% over FCC-OX-1.

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