Reuse of Spent FCC Catalyst for Removing Trace Olefins from Aromatics

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Pretreatment of spent FCC catalyst and its application in remove trace olefins in aromatics were investigated in this research. The most effective pretreatment route of spent FCC catalyst was calcining at 700 °C for 1 h, washing with 5% oxalic acid solution in ultrasonic reactor and dried. Treated spent FCC catalyst was modified with metal halides, then to prepare catalyst to remove trace olefins in aromatics. X-ray diffraction, Pyridine-FTIR, N₂ adsorption-desorption and inductively coupled plasma optical emission spectrometer (ICP-OES) were used to investigate the pretreatment process. The result showed that the performance of the treated spent FCC catalyst was much greater than that of the spent FCC catalyst, which indicted the possibility and improvement of this research.

Key Words : Spent FCC catalyst, Ultrasonic reactor, Olefins, Modification

Introduction

This paper described some potentially interesting results on the re-use of spent FCC catalyst for the removal of olefins from an essentially feed and the theme is of interest because the application or re-use of spent FCC catalyst is so important for environment concerns.

The amount of spent FCC catalyst discarded as solid waste has increased significantly in recent years due to the great demand for lightly and high quality transportation fuels as well as the changes in feedstock. Most of these spent catalysts have been disposed off as landfill in approved dump-sites. While metals such as Co, Ni, and V that present in spent catalyst are included in the list of hazardous wastes published in many countries, so disposal of these spent catalysts must accord with the environmental regulations. As a result of the stringent environmental criteria on spent catalyst handling and disposal, research on the process for recycling and reutilization of spent FCC catalysts has received considerable attention. Biorefinery of heavy metals and chemical leaching methods with mineral acids (sulphuric and nitric acid) and organic acids (citric, oxalic and gluconic acid) as well as mixture of organic acids were used to explore the route to reclaim the metals in the spent FCC catalyst. Utilization of spent catalyst as raw materials in the production of other valuable products is an attractive option, with taking the environmental regulations and economical profits into consideration. Spent fluid catalytic cracking (FCC) catalysts have been successfully utilized in cement production, clay-based products, preparation of Ultrafine Y-zeolite, act as supports for Fe-based catalysts with the goal of improving the attrition resistance of typical F-T catalysts etc.

Previous research in our group was focused on exploring proper catalyst for aromatic refining, which used modified clay or synthesized zeolites to remove trace olefins in aromatics. In refinery, aromatic streams are obtained from catalytic reforming and thermal cracking while these streams usually contain trace olefins such as mono-olefins, multi-olefins and styrene. Olefins are quantified by the Bromine Index (BI) which is an indicator of the presence of olefinic bonds. These olefins must be removed for their negative effect on the following process. Clay treatment have been widely used for removing trace olefins from aromatics with the drawbacks of limited lifetime and the used clay could not reuse except discard as solid waste. A growing awareness of environmental protection in the chemical industry asks for finding an efficient and cost-effective method to remove olefins in aromatics.

In the present work, spent FCC catalyst was used as raw material, treated with a route of calcination, acidic washing and modification so as to remove trace olefins in the aromatics. The objective was to explore a proper route to convert the spent FCC catalyst into useful catalyst in aromatic refining, which could provide a new way for disposal and recycle of the spent FCC catalyst.

Experimental

Pretreatment of Spent FCC Catalyst. The spent catalyst, Y-zeolite, was obtained from commercial FCC units in Chang-Ling refinery. The content of Ni, Co, V deposited on the spent catalyst was 0.98%, 0.22% and 0.042% (w/w) correspondingly. BET surface area and carbon content was 91.01 m²g⁻¹ and 0.218%. Figure 1 shows the scheme of the whole experiment process. Spent catalyst was firstly calcined at 973 K, washed with different solutions in ultrasonic reactor, dried at 393 K, at last the treated spent catalyst was ed at 973 K, washed with different solutions in ultrasonic reactor, dried at 393 K, at last the treated spent catalyst was used to explore the removal of trace olefins in aromatics.

The commercial clay was produced in Zhejiang province, China. Its component was shown in Table 1.
Catalyst Characterization. X-ray Diffraction (XRD) of the representative samples were operated on a RigakuD/ max-2000 equipment with Cu Kα radiation (λ = 0.15406 nm), using a generator voltage of 40 kV and a current of 30 mA, and a step of 0.04° at a rate of 2° per minute in the range from 5 to 65. The BET surface area, total pore volume and micropore volume of samples were calculated by the data of N₂ adsorption and desorption isotherms which conducted on Micromeritics ASAP 2010. The surface acidity was investigated by the adsorption of pyridine on the solid surface of samples. Prior to pyridine adsorption, sample wafers were evacuated at 753 K under high vacuum, and then followed by pyridine adsorption at room temperature. At last the wafers were desorption at 473 K. The FTIR spectra were recorded using a FT-IR6700 spectrometer on sample wafers.

Laboratory Experiment. Figure 2 shows the flowchart of laboratory experiment. The evaluation of the catalyst was carried out in a fixed-bed tubular microreactor, equipped with a constant-flow pump to control flow rate and a controlled heating system to maintain the temperature. The treated catalyst was packed between two quartz sands (40-60 mesh) and inserted into the reactor. The reaction was carried out under the following conditions: reaction temperature 448 K; reaction pressure 1 MPa; weight hourly space velocity (WHSV) at 15 h⁻¹. Samples of the inlet and effluent liquids in and out from the reactor were analyzed with the bromine index analyzer every 20 minutes. The value of olefin conversion (X) = [(n₀−n₁)/n₀] × 100, where n₀ is the initial content olefins and n₁ is final content of olefins. The aromatics were obtained from bottom of the naphtha reforming column in Sinopec Zhenhai Refining and Chemical Company Limited. The bromine index was about 1000 mgBr/100 g and the components of the aromatics were shown in Table 2.

Results and Discussion

Pretreatment. Temperature of Calcination: As shown in the Figure 3, the spent catalyst shows very poor performance, this mainly correlate with the coke, which could temporarily deactivate the active sites by poisoning and pore blockage. The conversion of olefins was greatly improved as the calcination temperature increased from 500°C to 700°C, this may explained by the combustion of coke lead to the addition of active sites, while the relatively lower performance at 500°C and 600°C may be attributed to the presence of some coke inside the pores of catalyst because of the lower calorific intensity. Conversion at 800°C was slightly lower than that of at 700°C, may owing to the collapse of the structure of the catalyst.²¹

Washing in Different Mediums: In Figure 4, different washing mediums on the performance of the spent FCC catalyst in removal of olefins were investigated. Among these washing solutions, spent catalyst treated with oxalic acid and citric acid showed best performance in experi-
ments. Spent catalyst washed with soda after calcination showed the lowest activity, this may due to the alkaline metals which could neutralize the acidic sites in the catalyst. Oxalic acid and citric acid could improve the performance of spent FCC catalyst in the experiment may owing to the use of oxalic acid and citric acid could enhance the metal removal through chelation reactions.\(^{5,22}\)

**Washing in Different Concentrations of Oxalic Acid Solution:** Figure 5 shows different concentrations of oxalic acid solution on the performance of spent FCC catalyst in the removal of olefins. Contrast experiments were conducted with four concentrations of oxidized oxalic acid solution. Results of conversion of olefins indicate that spent catalyst washed with 5% concentrations of oxalic acid had better performance than the other three ones. So the concentration of oxalic acid should be neither too low nor too high to wash the spent catalyst. The 5% is the proper content in this research.

**Comparison Between Washing with Ultrasonic Reactor and Magnetic Stirring:** Figure 6 shows the performance of spent catalyst treated with different process. The result indicates that spent catalyst treated with ultrasonic reactor showed an advantage in removing the olefins in aromatics. This may owing to the cavitation\(^{23}\) which could cause acoustic streaming (liquid circulation), high shear stress near the bubble wall, formation of micro-jets near the solid surface of the spent catalyst, generation of highly reactive free radicals and turbulence. As a result of the cavitation, the solvable compound and unstable materials deposited at the surface or inside the catalyst could be removed.

**Modification of Spent Catalyst.** After a series of pre-treatment process: calcining at 973 K, washing with 5% oxalic acid in ultrasonic reactor and then oven-dried, in order to make full use of the spent catalyst and strengthen its performance in aromatic refining, metal halides was loaded on the catalyst to adjust the acidic properties. In order to determine the content of metal halides, catalysts loading with metal halides vary from 1 to 10 wt % were tested. As shown in Figure 7, the modification was significantly improved the activity of spent catalyst. It was observed that the conversion of olefins was enhanced with increasing the metal halides loading on the treated spent catalyst support, but further increase the amount up to 10 wt % did not lead to an improvement in the activity. It may result from that metal halides tends to deposit at the pore mouths which causes blockage of the channels in the support, and consequently restricts the diffusion of reactants to the active sites within...
It was well known that the alkylation of aromatic with olefins over solid acid catalyst via the generally accepted carbenium ion mechanism illustrated in Scheme 1. On the basis of this mechanism, the olefins molecule was protonated by the B acid sites or L acid sites to a carbenium ion that generated, by electrophilic attack on the aromatic π-electrons, a mono or polyalkylbenzenium ion. The loss of the proton given the alkylated aromatic and restored the B acid sites and the L acid sites.

Characterizations of Different Samples in Pretreatment Process. A (spent FCC catalyst), B (spent FCC catalyst calcined at 973 K for 1 h), C (spent FCC catalyst calcined at 973 K for 1 h, washed with 5% oxalic acid with magnetic stirring), and D (spent FCC catalyst calcined at 973 K for 1 h, washed with 5% oxalic acid in ultrasonic reactor), were as representative samples to investigate the properties of the spent catalyst.

XRD Analysis: Figure 8 shows the XRD diffraction patterns obtained from A, B, C and D. All the diffraction patterns showed the peaks related to Al₂O₃ supported at diffraction angle 2θ = 45.9, 15.7°. The three diffraction patterns at diffraction angle 2θ = 21.5, 23.8, and 26.9° are related to the SiO₂ in the spent catalyst. So Figure 8 indicated that the treatment process did not change the structure of the spent catalyst.

Pyridine FTIR Spectra of Samples: The infrared spectra of pyridine adsorbed on the different samples at 473 K are shown in Figure 9. The band at 1540 cm⁻¹ suggests the present of Brønsted (B) acid sites, the 1450 cm⁻¹ band results from pyridine interacted with Lewis (L) acid sites, another band in this spectrum at 1490 cm⁻¹ arises due to contribution of both Lewis and Bronsted acid sites. Table 3 shows the amount of the total acid, total L acid, total B acid of these samples. The total acid amount of D is 1.56 × 10⁻⁴ mol·g⁻¹; A is 1.317 × 10⁻⁴ mol·g⁻¹, C is between A and D. As shown in Table 3, all the samples possess much more B acid sites than that of L acid sites, this may attribute to the components of the FCC catalyst. The active component in the FCC catalyst is mainly consisting of HY zeolite, REY or Y zeolite, which could provide B acid sites. As shown in (b),
as the metal halides loading on the treated spent catalyst increased from 3 wt% to 10 wt%, there was an increase in the total acid and the L acid, however, the increase in active metal halides resulted in the decrease of B acid. This was accord with the catalytic activity; the increase in the conversion of the olefins was apparently due to increase in the total acids sites, especially with the addition of L acid. So the different performance of the modified catalyst on olefins conversion may be caused by the diverse in L acid site. After modification, the amount of L acid site was increased as the amount of metal halides added, so as to olefins conversion. While further increase the metal halides to 10 wt% lead to the decrease in reaction activity, this is because the rapid reaction on the acid sites leads to the coke on the catalyst, and D. The BET surface areas of A decreased from 91.02 m²·g⁻¹ to D (82.48 m²·g⁻¹) after treatment, the average pore diameter increased from 5.53 to 6.74 nm, pore volume ranged from 0.1248 to 0.1383 cm³·g⁻¹. The increase in pore diameter may attribute to the cavitation in the ultrasonic reactor. When spent catalyst was treated with oxalic acid solution, solvable compound or unstable materials in the pore of the catalyst could be removed from the mesopore or large pores, while the stable metal compounds such as NiAlO₃, vanadyl species deposited at surface of catalyst could block the micropores and hard to remove. Furthermore, the removal of the solvable compound and unstable materials could also lead to loss in surface area; because the packing between these materials in the mesopore, large pore or at surface of the catalyst was partial contributed to the surface area. Sample D revealed great advantage over Sample A in removal trace olefins in aromatics. On one hand, D possessed more acid sites that could catalysis olefins alkylation or polymerize with aromatics, on the other hand, the larger pore volume in sample D could strengthen its adsorptive capacity to olefins.

Table 3. Acidic properties of sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total L acid (× 10⁻⁴ mol·g⁻¹)</th>
<th>Total B acid (× 10⁻⁴ mol·g⁻¹)</th>
<th>Total acid (× 10⁻⁴ mol·g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>0.050</td>
<td>1.267</td>
<td>1.317</td>
</tr>
<tr>
<td>C</td>
<td>0.021</td>
<td>1.317</td>
<td>1.338</td>
</tr>
<tr>
<td>D</td>
<td>0.008</td>
<td>1.552</td>
<td>1.560</td>
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<tr>
<td>3%</td>
<td>0.947</td>
<td>0.693</td>
<td>1.640</td>
</tr>
<tr>
<td>5%</td>
<td>1.380</td>
<td>0.386</td>
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</tr>
<tr>
<td>7%</td>
<td>1.842</td>
<td>0.089</td>
<td>1.931</td>
</tr>
<tr>
<td>10%</td>
<td>2.472</td>
<td>0.138</td>
<td>2.611</td>
</tr>
</tbody>
</table>

Conclusion

The treated spent FCC catalyst could be used to remove trace olefins in aromatics.

1. The optimal pretreatment of the spent FCC catalyst should be as follows: calcined at 973 K for 1 h, washed with 5% oxalic acid solution in ultrasonic reactor, and then dried.

2. The great olefin conversion of the spent FCC catalyst after pretreatment and modification showed one potential method on the re-use of the spent FCC catalyst which satisfies the environmental request.

3. Characterization of the treated spent FCC catalyst indicated that the pretreatment did not change the structure of the spent catalyst, the increase in total acid sites and pore volume after treatment was the main reason for the improvement of activity of the spent FCC catalyst.

References


