REDUCTION OF AROMATICS CRACKING ON ALUMINA BY PYRIDINE ADSORPTION

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Abstract

γ-Alumina is often used as a support in large number of reactions and has also inherent uses of its own. When γ-Alumina is used in catalytic reactions, undesirable side reactions such as cracking, isomerization and coke formation always exist. These give undesired products and lead to catalyst deactivation. Pyridine has been found to chemisorb readily on Lewis acidic sites. Monolayer chemisorptions even at ambient temperatures were observed. The steric effects of pyridine may be utilized. This is similar to bimodal pore distribution in which constrictions at the openings inhibit diffusion of large asphaltenic, coke producing molecules, whereas smaller reactants compounds have easy access. In this experimental work, aromatics' cracking was carried over untreated alumina and pyridine pretreated alumina. BTX traces in nitrogen fed over packed beds of untreated alumina and pyridine-treated alumina for the same reaction conditions and for the same duration of time. The experiments produced fixed carbon in spent catalyst 40% less in the pyridine pretreated alumina compared to untreated alumina. This indicates that aromatics cracking have been reduced by the pyridine adsorption.

Introduction

Originally pyridine was used to neutralize acidic sites on alumina for the sake of measuring quantitatively the number and strength of acidic sites [1, 2]. However, in this work pyridine is used to selectively poison the Lewis acidic sites and hence effectively reduces excessive coking which otherwise occurs. Typical examples of selective poisoning have been described in literature [3-6]. This research was designed to study aromatic cracking, particularly toluene and xylenes, that tend to crack over alumina producing carbon. Aromatics traces in nitrogen were fed over packed beds of pyridine-treated alumina and untreated alumina for the same reaction conditions and for the same duration of time of one week.

Coke Formation And Aromatics Cracking

A correlation was noted between the basicity of various aromatics compounds and the formation of coke in catalytic cracking [7]. A relationship would be expected because of the acid nature of cracking catalyst. It certainly appears that polyaromatics are important producers of coke [8]. In general, materials that have a higher ability for hydrogen transfer produce less coke.

In 1985, Goodboy et al. [9] found that cracking occurs preferentially on Lewis acid sites and that carbon clustering coincides with areas of Al^+. They observed that as carbon builds up on the catalyst, the rate of cracking decreases as the Lewis acid sites are blocked.

It is concluded that coke formation increases with increasing acid strength and acid-site density [10, 11]. The reduction of these two factors leads to decreased rates of coke formation. The main feature of cracking alkyl aromatics is the great stability of the phenyl ring and the relative ease of chain removal by dealkylation in a carbonium ion type mechanism [12].

Blocking Lewis Acidic Sites

Pyridine has been found to chemisorb readily on Lewis acidic sites preferentially and irreversibly. Monolayer chemisorptions even at ambient temperatures have been observed. Pyridine interacts with acidic oxides in specific way to form the coordinated species PyL on Lewis acid sites and the pyridinium ion PyH+ on protonic sites. Knozinger and Stolz in 1970 [13], found from infrared spectroscopy that pyridine was held by Lewis acid sites under their experimental conditions. It appears that Lewis sites retain pyridine between 150 and 550 °C The steric effects of pyridine may be utilized to improve the specificity of poisoning by restricting the adsorption of aromatics and reducing their accessibility to cracking sites, thus reducing cracking [14].

Experimental

A. Apparatus

The apparatus is composed of nitrogen cylinder, pressure regulator, gas rotameter, two saturators, two needle valve regulators, and a refrigerated constant temperature bath with a mixer and temperature controller.

B. Reactor Assembly

The reactor is made of 2.54 cm inside diameter, 25.4 cm long pyrex glass tube. A brass cylinder surrounds the reactor with three heating elements inserted at 120 degrees apart supplying the heat to the reactor. A thermocouple was inserted between catalyst pellets, and a temperature indicator and temperature controller were provided. Activated alumina 6-8 mm spherical pellets were stacked in the reactor to fill a 15 cm length of the packed bed reactor. Catalyst used was about 30 grams.

C. Procedure

Nitrogen was bubbled through two separate saturators in parallel containing (1) toluene and (2) xylenes at a total flow rate of 200 cc/min. Benzene was not tested because of its known resistance to cracking. The saturators were immersed in a refrigerated bath to keep the vapor pressure low so that a concentration of about 0.1% of aromatics in the gas stream was attained, which is of the order of 1000 ppm.

Pyridine treated alumina was obtained by bubbling nitrogen through pyridine liquid while maintaining the alumina at 100° C for two hours. Then the catalyst was desorbed at 400°C for three hours before reacting alumina with aromatics at a constant temperature of 320°C. Initially aromatics cracking were evaluated on the untreated alumina, and then cracking

was carried out on the pyridine treated alumina. Each test ran continuously for one week. At the end of this period, the catalysts were removed from the reactor and evaluated for their fixed carbon content.

Results And Discussions

The weights of carbon on samples of fresh, pyridine-treated and untreated catalysts are shown in Table 1. The results indicate that a reduction in carbon deposition of about 40% was found on the pyridine pre-treated alumina catalyst. This indicates that pyridine has neutralized some of the acidic sites on the alumina and has led to reduced aromatics cracking. The weight of carbon in the fresh catalyst was subtracted from the reported carbon values in both pyridine treated and untreated catalysts.

Analysis of total carbon in samples was carried by heating at 300 ^{0}C in an oven with air flow of 100 cc/min to get rid of toluene, xylene and pyridine. Then, samples were combusted at 1200 ^{0}C in presence of oxygen. The resulting carbon dioxide was measured by the calorimetric titration. The total carbon will include any carbonate-carbon present in the fresh or spent catalysts.

Chemisorption/adsorption studies of pyridine on alumina conducted on the Cahn Balance showed that pyridine remained adsorbed on alumina even in small quantities while desorbed with He flow at 400 ^{0}C (Table 2).

Conclusions

The experiments produced fixed carbon in spent catalyst 40% less in the pyridine pretreated alumina compared to untreated alumina. This indicates that pyridine activated alumina by reducing number of Lewis acid sites. Consequently, the catalyst did not promote aromatics cracking and therefore coking was reduced.

REFERENCES

[1]   Goldstein, M.S., *Experimental Methods in Catalytic Research*, R.B. Anderson, Ed.; Academic Press, New York, 1968; p.361.
[2]   Tanabe, K.; Misono, M.; Ouo, Y.; Inui, T., *New Solid Acids and Bases: Their Catalytic Properties* Elsevier, Amsterdam, 1989.
[3]   Pines, H. ; Haag, W.W., *J. Amer. Chem. Soc*. **1960,** 82, 2471.
[4]   Beranek, K.; Kraus, M.; Kochloefl, K.; Bazant, V. Actes Congr. Int. Catal. 2nd, Paris, **1** (1961) p.749.
[5]   Rosynek, M.P.; Smith, W. D.; Hightower, J. W., *J. Catal.* **1971**, 23, 204.
[6]   Rosynek, M.P. & Hightower, J. W., Proc. Int. Congr. Catal. 5th, Palm Beach, Fla., **2** (1973) 851.
[7]   Appleby, W.G., Gibson, J.W. & Good, G.M., *Ind. Eng. Chem. Process Des. Dev.* **1962** 102(1).
[8]   White, P., *J. Hydrocarbon Process.* **1968**, 47 (5), 103.
[9]   Wojciechowski, B.W. & Corma, A. *Catalytic Cracking,* Marcel Dekker, Inc., 1986.
[10] Goodboy, K.P.; Louy, G.C.; Fleming H.L *Petroenergy '85*, Sept. 19, 1985.
[11] Moscou, L.; Mone, R. *J. Catal*., **1973**, 30, 417.
[12] Venuto, P.B., *Catalysis in Organic Synthesis*, G.V. Smith, Ed., Academics, New York, 1977.
[13] Knozinger, H.; Stolz, H., *Bensenges Phys. Chem*., **1970**, 74, 1056.
[14] Benesi, H.A., **J. Catal**. **1973,** 28, 176.

Table 1 : Fixed Carbon on Various Samples.

Sample #	Wt % Total Carbon	Average carbon Deposition Wt %
1. Fresh alumina catalyst	(A) 0.21 (B) 0.19	0.20
2. Alumina pretreated with pyridine.	(A) 0.362 (B) 0.360 (C) 0.355	0.359
3. Alumina untreated	(A) 0.4 (B) 0.44	0.47

Table 2: Chemisorption/Adsorption of Pyridine on Alumina Using the Cahn Balance

Task Detail	Weight mg	Concentration Pyridine g/g Cat
Regeneration @ 400C	411.55	0.0
Flow Pyridine @ 100C	437.5 ± 2.0	0.063
He Purge over particles @ 100C	425.7	0.034
He Purge over particles @ 200C	417.8	0.015
He Purge over particles @ 250C	416.8	0.013
He Purge over particles @ 300C	414.7	0.0076
He Purge over particles @ 350C	413.4	0.0045
He Purge over particles @ 400C	411.9	0.00085