



Catalytic activity of P-cymene cracking on silica-alumina catalysts  
by Baiwei Lin

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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Abstract:

Amorphous silica-aluminas are used as cracking catalysts in oil production. Many properties of silica-alumina materials affect the catalyst surface acidity, the types of active sites, the interfunction of acid sites, and the catalytic activity. Studying these properties will improve the fundamental development of amorphous acid catalysts. It will also be of interest to the bifunctional catalyst area.

The object of this study is to find relationships between catalytic cracking activity and alumina contents of catalysts, the correlation between cracking activity and different types of acid sites (Lewis acid site or Bronsted acid site), and the comparison of cracking activity and isomerization activity.

P-cymene was employed as a reactant to determine the extension of cracking reaction and catalytic activity over seven silica-aluminas with different alumina contents. Cracking activities measured at different temperatures gave the activation energy information and those measured at the same temperatures provided activity relations to acidity and alumina contents in the test catalysts.

P-cymene cracking reaction shows the maximum silica-alumina catalytic activity at about 25% alumina content. Cracking activity is found to be dominated mainly by Bronsted acid sites and by total acidity for low alumina-content catalysts. The similar activation, energies and rate constants for p-cymene cracking and o-xylene isomerization indicate that the two reactions are affected by the same kind of active sites and have reasonably similar reaction mechanisms. Bronsted acid sites definitely provide activity for both cracking and isomerization reactions. A mechanism for p-cymene cracking over silica-alumina catalysts is suggested.

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A thesis submitted in partial fulfillment  
of the requirements for the degree

of  
Master of Science  
in  
Chemical Engineering

MONTANA STATE UNIVERSITY  
Bozeman, Montana

May 1988

378  
6294

APPROVAL

of a thesis submitted by

Baiwei Lin

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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## ACKNOWLEDGMENTS

The author wishes to thank the faculty and staff of the Chemical Engineering Department at Montana State University for their guidance and assistance.

Thanks are extended to Dr. John Sears for his advice, encouragement, and support throughout the course of this research and thesis preparation.

The author also wishes to thank Dr. Johnny L. Golden for the use of catalysts which he prepared.

Thanks are also extended to Dr. Frank P. McCandless for the use of his equipment.

## TABLE OF CONTENTS

	Page
APPROVAL.....	ii
STATEMENT OF PERMISSION TO USE.....	iii
ACKNOWLEDGMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
ABSTRACT.....	xi
INTRODUCTION.....	1
Problems In This Area.....	1
Motivation of This Work.....	3
Objectives.....	4
LITERATURE SURVEY.....	6
Silica-Alumina Surface Structure.....	6
Bronsted Acid Site.....	6
Lewis Acid Site.....	7
Acidities On Silica-Alumina Catalysts.....	8
Distinguishing Two Types of Acid Sites.....	12
The Infrared Spectrum of Ammonia.....	15
The Infrared Spectrum of Pyridine.....	16
Other Surface Spectroscopies.....	18
Catalytic Activity.....	19
P-cymene Cracking Mechanism.....	27
EXPERIMENTAL.....	30
Catalysts For Cracking Reaction.....	30
Reactant For Cracking Reaction.....	31

TABLE OF CONTENTS--Continued

	Page
Equipment For Cracking Reaction.....	32
Saturator.....	32
Reactor.....	34
Analytical System.....	34
Heating System.....	37
Experimental Procedures.....	37
Blank Experiment.....	37
Reaction Experiment.....	38
Calculations.....	39
P-cymene Mass Flow Rate.....	39
P-cymene Conversion.....	40
Reaction Rate.....	40
Rate Constant.....	41
Problems In The Experiment.....	42
RESULTS AND DISCUSSIONS.....	43
System Parameters.....	43
Catalytic Activity For P-cymene Cracking.....	44
Effect of Acidity On Catalytic Activity.....	49
Effect of Total Acidity.....	50
Effect of Bronsted Acidity.....	53
Effect of Lewis Acidity.....	55
Comparison of Cracking and Isomerization.....	61
Catalytic Activity Comparison.....	61
Activation Energy Comparison.....	66
Kinetics and Mechanism Study For P-cymene Cracking.....	70
Kinetics Study.....	70
Mechanism Study.....	77
CONCLUSIONS.....	81
REFERENCES CITED.....	82
APPENDIX.....	85

## LIST OF TABLES

Table	Page
1. Specific Surface Areas of Silica-Aluminas [7].....	10
2. Acidities of SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> From IR Results [14].....	17
3. Properties of Silica-Alumina Catalysts [20].....	19
4. Product From P-cymene Cracking [22].....	28
5. Properties of Catalysts [9].....	31
6. Experimental Parameters.....	44
7. Product Distribution of P-cymene Cracking.....	45
8. Corrected Bronsted Acidity [9].....	54
9. Activation Energy Comparison.....	69
10. Peak Areas From P-cymene Cracking At 315°C.....	85
11. Activity Calculation For P-cymene Cracking At Unchanged Temperature.....	86
12. P-cymene Cracking Activity For Sample A-10 At Different Temperature.....	87
13. P-cymene Cracking Activity For Sample A-44 At Different Temperature.....	88



## LIST OF FIGURES

Figure	Page
1. Variation of cumulative acidity as a function of alumina content [7].....	11
2. Variation of amount of OH groups as a function of alumina content [7].....	13
3. Relationship of the strong acidity measured from chemisorption isotherms to the measured alumina contents of the catalysts [9].....	14
4. Relationship of catalytic activities to silica contents of silica-alumina catalysts [18].....	21
5. Relationship of entropies (relative maximum mobility) of adsorbed ammonia to silica contents of silica-alumina catalysts [18].....	22
6. Isobutane cracking activity of silica-alumina catalysts of varying Lewis acid group concentration [21].....	23
7. Comparison of the measured Bronsted acidity with catalytic activity from the data of Holm and Clark [14,18].....	25
8. Relationship of o-xylene isomerization rate at 300°C to the measured alumina contents of the test catalysts [9].....	26
9. Schematic diagram of experimental apparatus.....	33
10. Schematic diagram of the saturator.....	35
11. Schematic diagram of the Berty reactor.....	36
12. Relationship of reaction rate for p-cymene cracking at 315°C to the measured alumina contents in catalysts.....	47

ix  
LIST OF FIGURES--Continued

Figure	Page
13. Comparison of p-cymene cracking conversion with n-octane cracking conversion.....	48
14. Total acidity, Lewis acidity, and Bronsted acidity as a function of apparent alumina contents [14].....	51
15. Catalytic activity of p-cymene cracking as a function of strong acidity (from Golden).....	52
16. Catalytic activity of p-cymene cracking as a function of total acidity (from Schwarz).....	52
17. Catalytic activity of p-cymene cracking as a function of corrected Bronsted acidity (from Golden).....	56
18. Catalytic activity of p-cymene cracking as a function of measured Bronsted acidity (from Schwarz).....	56
19. Catalytic activity of p-cymene cracking as a function of measured Lewis acidity. (from J. A. Schwarz).....	57
20. Relationships of activity and acidity to the measured alumina contents in catalysts.....	59
21. Relationships of activity and acidity to the apparent alumina contents in catalysts.....	60
22. Conversions of p-cymene cracking and o-xylene isomerization as a function of alumina contents.....	62
23. Comparison of rate constants for p-cymene cracking and o-xylene isomerization.....	64

x  
LIST OF FIGURES--Continued

Figure	Page
24. Rate constants of p-cymene cracking and o-xylene isomerization as a function of acid desity. (from J. Golden's data).....	65
25. Arrhenius plot for sample A-10 in p-cymene cracking reaction.....	67
26. Arrhenius plot for sample A-44 in p-cymene cracking reaction.....	68
27. Experimental data for sample A-10 in p-cymene cracking reaction at 222°C.....	74
28. Experimental data for sample A-44 in p-cymene cracking reaction at 220°C.....	75
29. The conversion of apparent and measured alumina contents in silica-alumina catalysts.....	89
30. Experimental data for sample A-3 in p-cymene cracking reaction at 315°C.....	90
31. Experimental data for sample A-7 in p-cymene cracking reaction at 315°C.....	91
32. Experimental data for sample A-10 in p-cymene cracking reaction at 315°C.....	92
33. Experimental data for sample A-18 in p-cymene cracking reaction at 315°C.....	93
34. Experimental data for sample A-26 in p-cymene cracking reaction at 315°C.....	94
35. Experimental data for sample A-44 in p-cymene cracking reaction at 315°C.....	95

## ABSTRACT

Amorphous silica-aluminas are used as cracking catalysts in oil production. Many properties of silica-alumina materials affect the catalyst surface acidity, the types of active sites, the interfunction of acid sites, and the catalytic activity. Studying these properties will improve the fundamental development of amorphous acid catalysts. It will also be of interest to the bifunctional catalyst area.

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P-cymene cracking reaction shows the maximum silica-alumina catalytic activity at about 25% alumina content. Cracking activity is found to be dominated mainly by Bronsted acid sites and by total acidity for low alumina-content catalysts. The similar activation energies and rate constants for p-cymene cracking and o-xylene isomerization indicate that the two reactions are affected by the same kind of active sites and have reasonably similar reaction mechanisms. Bronsted acid sites definitely provide activity for both cracking and isomerization reactions. A mechanism for p-cymene cracking over silica-alumina catalysts is suggested.

## INTRODUCTION

Silica-alumina gel has long been used to make catalysts for cracking reactions in the petroleum industry. A lot of research studies have helped to elucidate characteristics of these catalysts, such as catalyst surface acidity, active site population and catalytic activity. But there are still many properties of silica-alumina materials which are not well understood.

Problems In This Area

In general, the silica-alumina catalyst has been observed to exhibit active sites which are suggested to be Lewis and Bronsted acidities with some apparent interconversion between the two types of sites. Some investigators believe that the cracking activity is only due to the Bronsted acid sites which are localized at the free hydroxyl groups on the surface. However, some cracking reactions have been found to correlate with the measurements of Lewis acidity. There is a disagreement over whether these active sites are Bronsted acid sites or Lewis acid sites.

Cracking reactions over a large range of alumina content in silica-alumina catalysts have been studied. With different alumina contents, the catalysts show variation of

acidities and cracking activities [7-18]. Bronsted acid sites and Lewis acid sites on silica-alumina surfaces have been distinguished by infrared spectroscopy with adsorption of ammonia and pyridine [9-15]. The maximum Bronsted-acid-site concentration occurs at about 25 percent alumina [14]. Similarly, measurements of some cracking reactions indicate a maximum silica-alumina catalyst activity at a bulk concentration of 15-25% alumina [18]. However, a satisfactory correlation between cracking activities and acidities has not been found. Some researchers suggest that the acid site strength seems to determine cracking activity more than acidity itself. Which one mostly determines the rate of cracking reactions is still unknown.

Some researchers formulated a simple mechanism of cracking based on a free-radical approach, which implies mostly thermal cracking [24]. Others suggested a carbonium ion mechanism in catalytic cracking, which could involve the Bronsted acidity [22]. Reactions involving carbonium ions include dealkylation, hydrogenation, isomerization, and polymerization. In the study of hydrocarbon cracking mechanism, the tracer technique using  $^{14}\text{C}$  was adopted [23] and with the observed product distribution found in cracking reaction, it is still possible that Lewis acid sites directly or indirectly contribute activity to carbonium ion formation, e.g., to initiate a cracking reaction.

### Motivation of This Work

Silica-alumina materials provide a perfect system for variation of acidity, ranging from very weak acids to very strong acids. The extensive background concerning silica-alumina makes the system ideal for a fundamental study of an amorphous solid surface. Though largely replaced by zeolites in the last few decades, amorphous silica-alumina catalysts are still used in the petroleum industry because of its better properties for heat transfer and diffusivity. Also, silica-alumina catalyst is a very important support for the metallic catalysts, such as a bifunctional hydrodesulfurization catalyst. This fundamental study will also be of interest to the area of such metallic catalysts.

J. Golden made a series of silica-aluminas with different alumina contents and studied their surface area, acid site density, the quantity of strong acid sites and catalytic activity for o-xylene isomerization [9]. It has been observed in his study that the strong acid amounts are in good agreement with literature reports for both commercial and research silica-aluminas, which shows the maximum acid site strength occurs at about 25 percent alumina; the activity measurements of o-xylene isomerization on these catalysts show the catalytic activity is mostly consistent with the acid-site strength distribution, that is the activity for o-xylene

isomerization is basically affected by strong acid-site acidity. The relation between catalytic activity of isomerization and Bronsted acidity indicates that Bronsted acid sites are primarily the active point for O-xylene isomerization.

The present work is a related study based on J. Golden's research and wishes to find the relationship between catalytic cracking activity and alumina content for the same series of catalysts. The question arises as to which type of acid site, Bronsted acid site or Lewis acid site, is more active for the p-cymene cracking reaction. Therefore a correlation of cracking activities with Bronsted acid strength as well as Lewis acid strength needs to be studied and is attempted in this work. A comparison of cracking activity with previous o-xylene isomerization activity will be done to see if there is a general activity dependence on acidity. Also, mechanisms of p-cymene cracking will be analyzed based on the product distribution.

#### Objectives

The purpose of this research is to contribute to the fundamental understanding of amorphous silica-alumina catalysts. The objectives are:

Examine the cracking activity of p-cymene on silica-alumina catalysts with different alumina contents and



determine a relationship between cracking activity and alumina content in the catalysts.

Correlate cracking activity of silica-alumina catalyst with acid site strength and implied acid site types (Bronsted or Lewis acid site).

Compare the cracking activity results to previous o-xylene isomerization activity on the same catalysts (obtained from J. Golden's research work) and discuss activity dependence on the acidity.

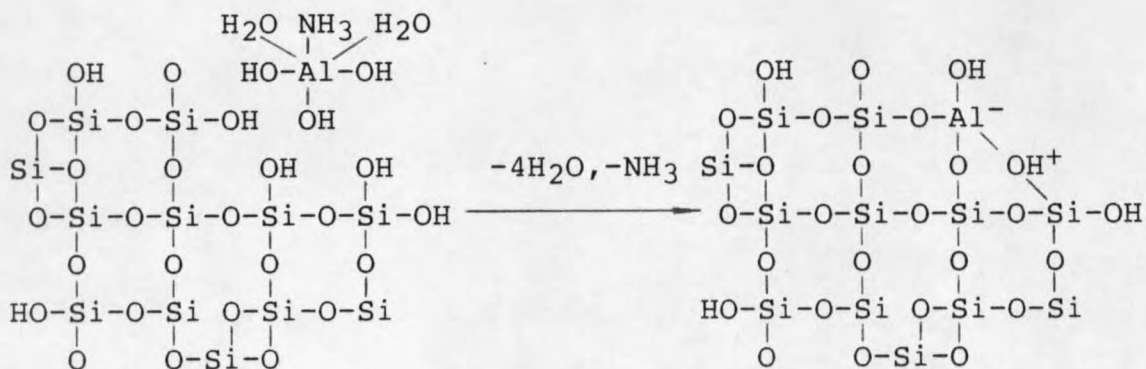
## LITERATURE SURVEY

Silica-Alumina Surface Structure

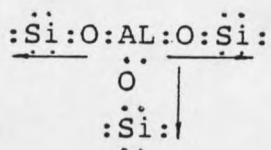
Neither silica nor alumina is an active cracking catalyst, but a cogelled mixture of silica and alumina containing mainly silica is highly active. The incorporation of alumina into silica, even at very low concentrations results in the formation of surface sites. At least some of those sites must be Bronsted and/or Lewis acid sites [1].

Bronsted Acid Site

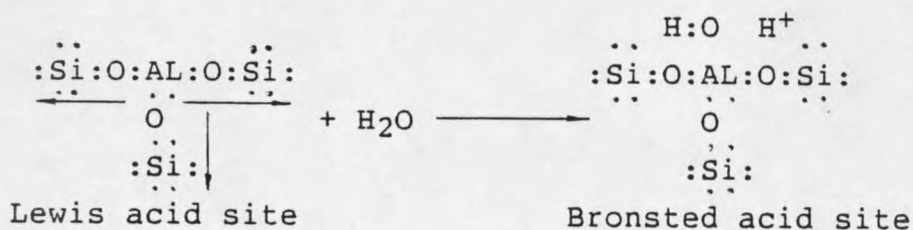
The OH groups terminating primary silica and alumina particles vary from weakly acids to strong acids (superacids) and show no cracking activity. The incorporation of trivalent aluminum ions into the silica surface produce surface OH groups having strong Bronsted acidity. The protonic acidity arises from the dissociative adsorption of H<sub>2</sub>O on the aluminum ion:



With the dissociation of water, alumina ions then tetrahedrally coordinate to oxide ions:



The strong electrophilic action of the aluminum ion is caused by the asymmetry of its position in the surface, where it is surrounded by quadra-valent silicon cations. Because of the asymmetry, the electronic charge is withdrawn from the aluminum ion to silica cations and make the alumina ion more positive. In this way aluminum ions develop a sufficiently strong field to acquire a hydroxyl group by splitting off hydrogen from water:

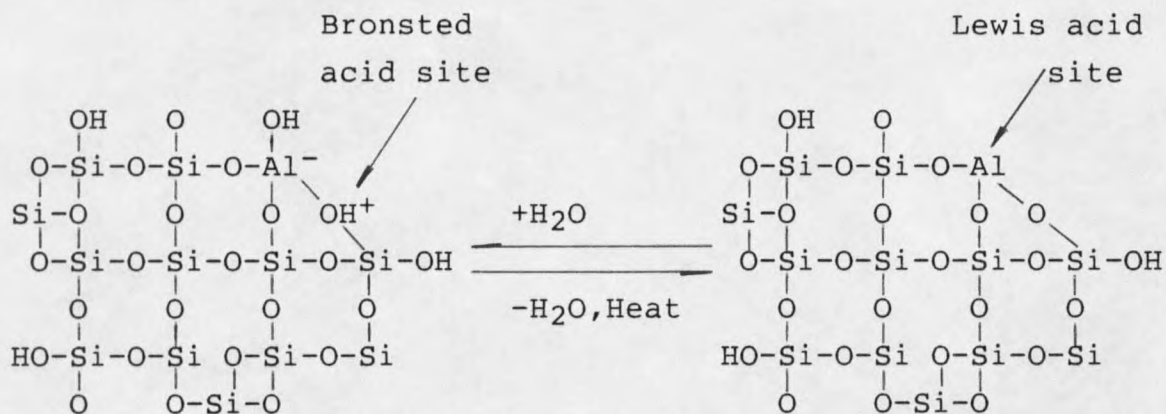


The structure of  $-\overset{\text{H}^+}{\text{Al}}-\text{O}-\text{Si}-$  group is strongly polarized by the asymmetry of aluminum ion which induces a strong acidity in the group.

#### Lewis Acid Site

When the silica-alumina surface is dehydrated by heating to high temperature, water is removed from the Bronsted site, exposing the aluminum ion with its electron-pair-

acceptor properties, thereby forming a Lewis acid site, as shown below:



Alumina atoms acquire an additional electron pair to complete its bonding. Thus if the probe gas has additional electrons to interact with the Lewis site, it can share an electron pair with the aluminum atom. Water molecules may be coordinated at the Lewis acid site to provide a source of protons. Such Lewis acid sites are converted quantitatively to Bronsted acid sites upon the addition of water and reversibly back to Lewis acid sites upon heating. The dehydrated surfaces can show Bronsted acidity, Lewis acidity, or both, depending on the pretreatment conditions.

#### Acidities On Silica-Alumina Catalyst

Alumina does not show significant Bronsted acidity at any observed calcination temperature. With the adsorption of ammonia or pyridine, alumina has no infrared bands of  $\text{NH}_4^+$

or pyridinium ion [2]. Although the OH groups on alumina do not show Bronsted acidity, alumina does show considerable Lewis acidity after calcination at relatively high temperatures. At elevated temperatures, dehydroxylation on the surface occurs and makes aluminum cations exposing an electron-pair-accepting nature after the OH groups have been removed. The concentration of the Lewis acid centers depends on treatment temperature [2,3].

Silica gel shows neither Bronsted nor Lewis acidity. Even at high temperature calcination, Lewis acidity is not observed [2,11]. From the infrared spectra of adsorbed pyridine, the Bronsted acidity of Si-Al materials increases with Si to Al ratio [4]. By introducing HF into silica gel, the Bronsted acid site is observed [5,6]. The Bronsted acid site appears because the charge induction through the oxygen-silica bridge to the fluorine atom, which increases the acidity of the neighboring O-H group. This effect occurs through the asymmetry of the surface and the strong charge-withdrawing characteristics of the fluorine. The electronic charge is pulled towards the fluorine and away from the O-H bond, making the O-H group a strong proton donor. This situation is similar to that involving an aluminum ion on the surface of a silica particle.

Fedorynska, et al. [7] investigated the acidity on silica-alumina surface as well as the concentration of surface hydroxyl groups. The catalysts were prepared by

hydrolysis of aluminum isopropoxide and ethyl ortho silicate. The catalyst surface areas are listed in Table 1.

Table 1. Specific Surface Area of Silica-Aluminas [7].

Al <sub>2</sub> O <sub>3</sub> content (mol %)	surface area (m <sup>2</sup> /g)
100	184
87	249
74	179
63	187
52	175
40	84
30	139
15	334
10	365
0	401

The distributions for amount and strength of acid sites were determined by titration in the presence of Hammett indicators. For a reaction of



The Hammett acidity function is defined as

$$H_0 = \log ( a_{H^+} \times f_B / f_{BH^+} )$$

where

$a_{H^+}$  --- the thermodynamic activity coefficient of  $H^+$

$f_B$  --- the activity coefficient of a base

$f_{BH^+}$  -- the activity coefficient of  $BH^+$

The catalyst samples were suspended in benzene and the change of Hammett indicator color marked the end point of titration. Fig. 1 presents the distribution of acid sites at various strengths. The strongest acid sites are due to those

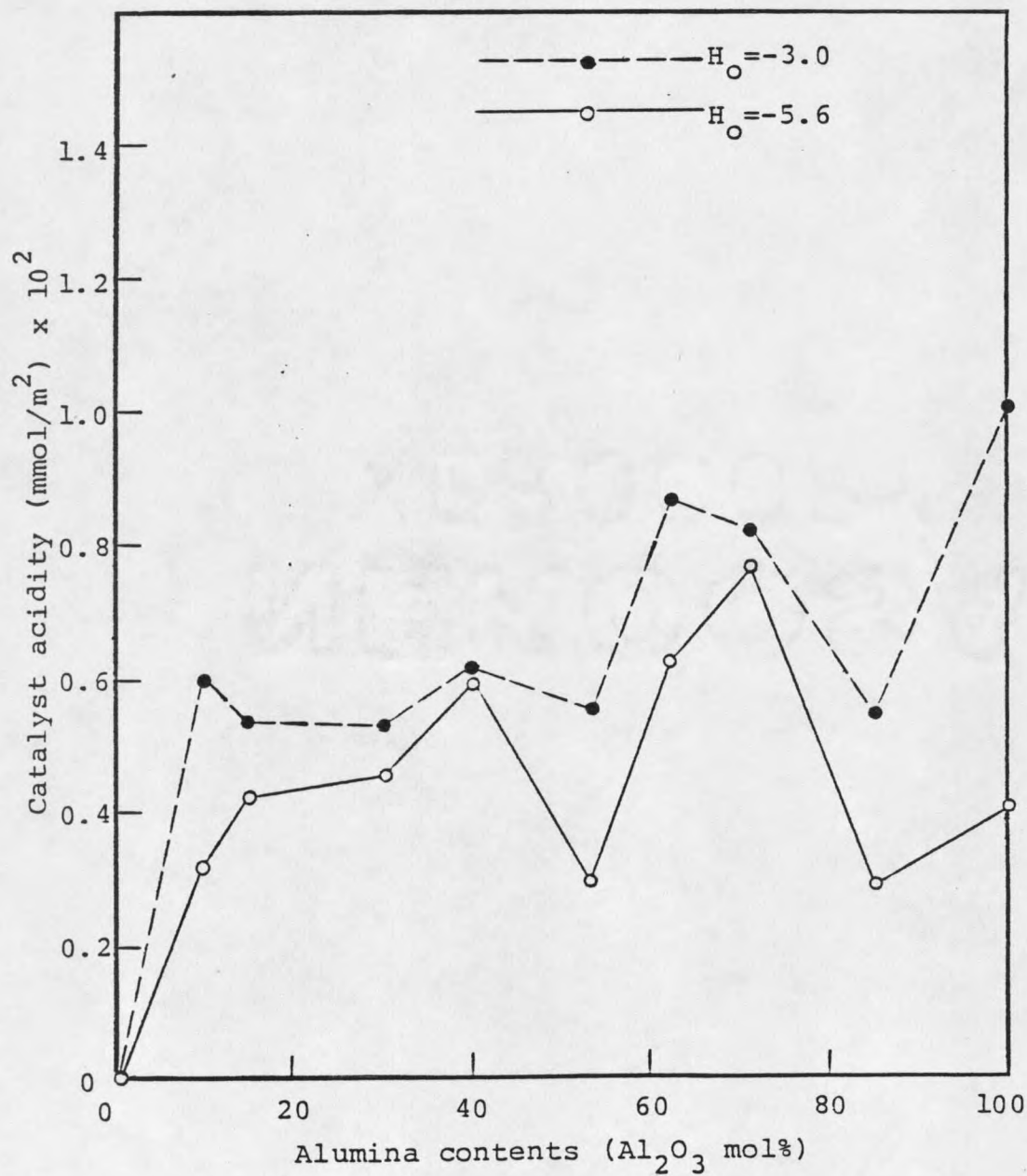


Figure 1. Variation of cumulative acidity as a function of alumina content [7] .

at acidity of  $H_0 = -5.6$ . The sample containing small quantity of  $SiO_2$  in  $Al_2O_3$  exhibits the strongest acid properties.

For determination of OH groups, Fedorynska adopted Shima's method [8] involving titration with ethyl dichloroaluminum. Fig. 2 [7] demonstrated the amount of surface OH groups determined by the reaction with the organoaluminum compound. The concentration of OH groups varies nonuniformly with the composition of the catalysts.

J. Golden used triethylamine (TEA) as a gaseous base adsorbate to determine the acidities of silica-aluminas [9]. The TEA was used because of its stability against dissociation and its character as a sterically hindered Lewis base [10]. Therefore TEA is probably difficult to coordinate with surface Lewis acid sites and the strong Lewis acid sites can be discriminated from strong Bronsted acid sites.

The CAEDMON program [9] was used to calculate TEA adsorption energy distribution in Golden's work. Two site energies (weak site energy and strong site energy) were observed on the test material surfaces. Strong acidity against alumina content is shown in Fig. 3.

#### Distinguishing Two Types of Acid Sites

Extensive work reported in the literature shows that the activity of cracking catalysts results from the presence of acid centers on the catalyst surface. However, there is





























































































































































































