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Silicoaluminophosphate-5 molecular sieve: Characterization and catalytic activity for alkylaromatic reactions

Castro, Albino, Ph.D.

Rice University, 1986
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SILICOALUMINOPHOSPHATE-5 MOLECULAR SIEVE:
CHARACTERIZATION AND CATALYTIC ACTIVITY FOR
ALKYLAROMATIC REACTIONS

by

ALBINO CASTRO

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

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Houston, Texas
October, 1986
Abstract
Silicoaluminophosphate-5 Molecular Sieve: Characterization and Catalytic Activity For Alkylaromatic Reactions
by
Albino Castro

Highly crystalline silicoaluminophosphate-5 (SAPO-5) was prepared according to a Union Carbide patent. This solid material was characterized by a number of physical techniques and used as a catalyst for several alkylaromatic interconversion reactions. Information about the reaction mechanisms and the active sites was provided by kinetic studies involving tracer molecules labeled with $^{13}$C and D isotopes.

The bulk composition of SAPO-5 (molar basis including only Al, Si, and P) was shown by neutron activation and atomic adsorption to be $(\text{Si}_{0.10}\text{Al}_{0.56}\text{P}_{0.34})\text{O}_2$. A fresh calcined sample had a BET surface area of $235\text{ m}^2\text{ g}^{-1}$. Although coking decreased the surface area during the reactions, it could be completely regenerated. X-ray analysis indicated that the structure of the catalyst was not affected by coking/regeneration cycles. The catalyst contained $1.3\times10^{14}$ \( \frac{\text{H atoms}}{\text{cm}^2} \) that could be readily exchanged. It is speculated that some of these H atoms serve as active sites for the alkylbenzene reactions.

Xylene isomerization was the primary reaction used to test the activity of SAPO-5 in a CSTR. While the three xylene isomers were the principle products observed in the temperature range 300-400°C, some disproportionation pro-
ducts (toluene and the three trimethylbenzenes isomers) were also observed. Xylene isomerization followed first order kinetics with observed activation energies for xylene interconversion in the range of $21-24 \text{ kcal/mole}$. The disproportionation reactions follow reversible second order kinetics with an observed activation energy of $8.5 \text{ kcal/mole}$.

The xylene isomerization reactions are primarily intramolecular. More than 90% of the m-xylene formed initially from mixtures of o-xylene and o-xylene labeled with $^{13}$C in the methyl groups was either completely unlabeled or labeled. However, at higher conversion where disproportionation becomes significant, intermolecular scrambling increases.

While aryl hydrogens are extremely labile under these conditions, the hydrogens in the methyl groups are relatively inert. Even at short contact times, the ring hydrogens of mixtures of perdeuterated and unlabeled o-xylene exchanged to statistical equilibrium, whereas the methyl groups remained either fully labeled or unlabeled. It was shown, however, that during isomerization one H (or D) atom was exchanged on the average in the migrating methyl group.

The activities of other acidic oxide catalyst (amorphous silica-alumina, ZSM-5, and AlPO-5) were compared with SAPO-5. It was concluded that all exhibit similar types of catalytic behavior with the rates varying over several orders of magnitude and ZSM-5 being the most active.
Acknowledgments

I would like to express my sincere thanks to the following persons and companies for their contributions to this work:

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Mr. Alan Penock for help in machining several important pieces of apparatus used in my work.
Dr. Paul Schipper of Mobil's Paulsboro Labs for arranging for the atomic adsorption measurements to be run on my synthesized SAPO-5.

The National Science Foundation Graduate Minority Fellowship, the GEM Foundation Fellowship, the Minnie Stevens Piper Fellowship, and the National Hispanic Scholarship Fund for providing financial assistance during this work.

Mr. Fransisco and Mrs. Eugenia Castro, my parents, for their love, encouragement and guidance throughout my life.

Miss Gloria Cortez, a special friend, for providing me with many opportunities to smile and be thankful.
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<td>a</td>
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<td>Coking factor, observed rate over initial rate</td>
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<tr>
<td>a&lt;sub&gt;i,k&lt;/sub&gt;</td>
<td>----</td>
<td>Number of atoms of kth element in compound i</td>
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<tr>
<td>A&lt;sub&gt;k&lt;/sub&gt;</td>
<td>----</td>
<td>Total weight of kth element in system</td>
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<tr>
<td>C</td>
<td>mole/liter</td>
<td>BET (slope/intercept +1)</td>
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<tr>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
<td>mole/liter</td>
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<td>C&lt;sup&gt;o&lt;/sup&gt;</td>
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<td>D&lt;sub&gt;eff&lt;/sub&gt;</td>
<td>cm²/s</td>
<td>Effective diffusivity</td>
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<td>Mole fraction of isomer with i D atoms</td>
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<td>D&lt;sub&gt;p&lt;/sub&gt;</td>
<td>cm</td>
<td>Average particle diameter</td>
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<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
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<td>G</td>
<td>g·m/s·cm²</td>
<td>Fluid superficial velocity</td>
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<td>k&lt;sub&gt;d&lt;/sub&gt;</td>
<td>s⁻¹</td>
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<td>mole/g·s·torr</td>
<td>Rate constant for ith reaction</td>
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<td>n&lt;sub&gt;bz&lt;/sub&gt;</td>
<td>number/pulse</td>
<td>Number of benzene molecules per pulse, 1.36×10&lt;sup&gt;19&lt;/sup&gt;</td>
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<td>n&lt;sub&gt;i&lt;/sub&gt;</td>
<td>moles</td>
<td>Moles of i at equilibrium</td>
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\[
\begin{array}{ll}
\text{n}^\circ & \text{mole/hr} \\
\text{Re} & \text{Modified Reynolds' number} \\
\text{P} & \text{torr/tra} \\
\text{P}_i & \text{Partial pressure of compound i} \\
\text{P}^\circ & \text{Feed partial pressure of compound i} \\
\text{P}_o & \text{Saturation partial pressure of nitrogen} \\
\text{R} & \text{torr} \\
\text{R} & \text{Gas Constant or} \\
\text{mol} & \text{kmole-}K \\
\text{R} & \text{Recycle ratio or} \\
\text{cm} & \text{Particle Radius} \\
\text{r}_i & \text{mole} \\
\text{g.s} & \text{Observed rate of reaction} \\
\text{r}^\circ & \text{mole} \\
\text{g.s} & \text{Initial rate of reaction} \\
\text{T} & \text{°C} \\
\text{t} & \text{sec} \\
\text{t} & \text{Time on stream} \\
\text{t} & \text{sec} \\
\text{t} & \text{Mean residence time for plug flow} \\
\text{V} & \text{cc(STP)} \\
\text{V} & \text{Volume of nitrogen adsorbed} \\
\text{Vr} & \text{cc} \\
\text{Volume of reactor} \\
\text{Vt} & \text{cc(STP)/hr} \\
\text{Total volumetric flow through reactor} \\
\text{W} & \text{gm} \\
\text{Weight of catalyst} \\
\text{X} & \text{----} \\
\text{Conversion} \\
\text{X}_e & \text{----} \\
\text{Equilibrium Conversion} \\
\text{\eta} & \text{torr.g.s} \\
\text{mole} & \text{Modified CSTR space time system or} \\
\text{----} & \text{Effectiveness factor} \\
\text{\lambda}_k & \text{----} \\
\text{Lagrange multiplier of element k} \\
\text{\mu} & \text{Poise} \\
\text{Fluid viscosity}
\end{array}
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<td>$\frac{\rho}{cm^3}$</td>
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I. Introduction

Molecular sieve zeolites are crystalline microporous aluminosilicates which are based on infinitely extending three dimensional networks of $\text{AlO}_4^-$ and $\text{SiO}_4$ tetrahedra linked to each other by sharing all of the oxygens (1). The tetrahedral coordination of the trivalent Al atom results in a net negative charge that must be balanced by a cation. Smith (2) stated that "a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration." It is the ion-exchange capability that allows the replacement of the large cations with hydrogen ions to form catalytically active solid acid surfaces both outside and within the cavities of these structures. To balance the negative charge, the exchanged hydrogen ions bond with oxygens adjacent to the aluminum to form OH groups, which are potential Brønsted acid sites.

The pore geometry differs greatly from one zeolite to another (1). The pore dimensions are determined from the rings of 4, 6, 8, 10, or 12-tetrahedra forming the entrances to the pores. For example, the structures of $\Lambda$, $\chi$, and $\gamma$ are shown in Figure 1. The silica and alumina tetrahedra are joined together to form a cuboctahedron. This structure, taken from reference 3, is also known as a sodalite
Sodalite Unit

Type A Zeolite

Type X(Y) Zeolite

Figure 1
unit or truncated octahedron. It contains twenty-four tetrahedra arranged to form six four-sided and eight six-sided faces. Since the larger of the two possible entrances to this structure is made up of rings containing six tetrahedra, the resulting 2.6 Å opening is so constraining that only a few very few molecules (e.g. H₂O...) can enter. Generally no catalysis occurs inside these cavities. Zeolite A, Figure 1, is formed when the sodalite units are connected by four bridge oxygens between the square faces. Zeolites X and Y, Figure 1, are formed when the hexagonal faces are connected with six bridge oxygen atoms.

Names of the zeolites are related to the state of the charge balancing cation (1). If the zeolite is ion exchanged with Na⁺, it is called Na zeolite. When exchanged with Ca²⁺, it is labeled Ca zeolite, etc. The H form results when all or most of the exchangeable cations are H⁺'s. Combinations are possible for partially exchanged species, i.e. NH₄Na zeolite. Probable positions of the charge-balancing cations are exactly defined. Some compilations of their actual location based on powder x-ray analysis exist (4); however, they are dependent upon the exchange level, degree of calcination, etc. and would vary from one catalyst to another.

For X and Y zeolites, Smith (1) has defined five different sites, as illustrated in Figure 2. There are sixteen I sites per unit cell located in the center of the hexagonal
Exchangeable Cation Site Locations in X and Y Zeolites

Figure 2
prism formed by the six bridge oxygen atoms. Inside the sodalite unit opposite from site I are sixteen I' sites per unit cell. Type II sites are located just outside the unjoined hexagonal faces of the sodalite units. There are thirty-two such sites. An additional 32 type II' sites are located inside the sodalite unit opposite of the type II sites. Type III sites are outside the hexagonal prisms and the sodalite units near the four membered rings in the pore entrances to the unit cell.

There are thirty-four natural zeolites and over one hundred synthetic zeolites (3). The major use for natural zeolites is in bulk mineral applications, i.e. paper filler, aggregates, fertilizers, and cement filler (5). The first major industrial use for synthetic zeolites was the introduction of X zeolite in catalytic cracking in 1962 (5). Milton (6) has reviewed the beginnings of molecular sieve zeolites in 1967. More recent review articles (3,7) on the applications of zeolites as catalysts indicate their continued importance in hydrocarbon conversions.

Coupled with this utilization (8) has been much zeolite research activity. Crystallinity offers the possibility of structure-reactivity correlations. For example, since the hydrogens of the -OH groups are associated with the negative charge of the aluminum, one can change the surface acidity by varying the aluminum content and thereby placing the
hydrogens in different sites. By varying the aluminum content, one can alter the "crystal field effects".

Many novel structures related to zeolites have recently appeared in the patent literature. Some are formed by the simple replacement of either the silicon or aluminum atoms with another metal atom. Ratnasamy and Borade (9) have worked with ferrisilicate zeolites. Pyke (10) and Wilson (11) have looked at aluminophosphates.

Other structures involve the incorporation of a third element in the matrix. Messina et al. (12) have studied crystalline ferroaluminophosphates. Lok et al. (13) have examined titanium aluminophosphates. Silicoaluminophosphates have been investigated by Lok (14), Derouane (15), and Mitsubishi Chemical Industries (16). Bi-Al-Si oxides were studied by the New Fuel Oil Development Technology Research Association in Japan (17).

Also, a few structures with a quaternary composition have been synthesized. Lok et al. have investigated Fe-Al-P-Si (18), Co-Al-P-Si (19), and Zn-Al-P-Si oxide molecular sieves (20). All of these structures offer new ion exchange, adsorption, and catalytic possibilities.

One of these novel structures is the main focus of this research. With its three different tetrahedral atoms (Si, Al, and P), silicoaluminophosphate-5 does not fall under Smith's definition of a zeolite. Consequently, it will be referred to as a molecular sieve only. SAPO-5 was developed
concurrently by Union Carbide (13), Mobil Oil Corporation (15), and Mitsubishi Chemical Industries (16) and shares its structure (different from any known zeolite) with another novel molecular sieve AlPO-5 (21).
Objectives

The main objectives of this work were to synthesize the molecular sieve SAPO-5, to characterize it both physically and chemically, and to test its catalytic activity. Physical characterization involved confirmation of the crystalline structure and determination of the catalyst surface area. Compromising the chemical characterization was determination of the bulk composition and identification and quantification of the catalytic sites. Further characterization involved the development of a kinetic description and mechanism for a model reaction over the catalyst. As a model reaction, xylene isomerization was chosen.

A related objective was to compare the catalytic properties of SAPO-5 with other catalysts, viz. ZSM-5, AlPO-5, and amorphous Houdry M-46 silica-alumina, to determine if a general behavior pattern for xylene isomerization over solid acid catalysts could be made. These catalysts provided a variety of catalytic conditions for the isomerization reaction, i.e. amorphous (M-46) to crystalline structures (ZSM-5, SAPO-5, AlPO-5), low (AlPO-5) to high (SAPO-5) site concentrations, and medium (ZSM-5) to large (SAPO-5, AlPO-5) pore sizes.
Xylene Isomerization

General

Xylenes consist of three di-methylbenzene isomers. Para-xylene is 1,4-dimethylbenzene, ortho is the 1,2 isomer, and meta is the 1,3 isomer. These are also referred to as p-xylene, o-xylene, and m-xylene. The principal industrial source of xylenes is the C₈ aromatic fraction of petroleum naphtha reformate. Of the three, para-xylene is the most useful. However, ortho-xylene is also valuable. Unfortunately, the most thermodynamically stable isomer, m-xylene, is the least useful.

Hanson and Engel (22) in a 1967 AIChE article wrote the following:

Considerable interest has developed in recent years in the isomerization of xylenes, mainly because of a greatly increased demand for para-xylene as an intermediate in the manufacture of polyester fibers and films. ... The production of any particular isomer of xylene could be greatly increased by the isomerization of mixtures of xylenes, with subsequent separation of the desired isomer. Because of this, xylene isomerization processes are expected to become more attractive economically as the demand for para-xylene increases.

By 1985, xylenes as a group were ranked 26th in the list of the top fifty chemical produced in the United States (23). Para-xylene alone ranked 28th. In early 1986, the projected (24) production rate for p-xylene was about 90% of capacity.

There are several xylene isomerization patents (25-29). Most processes function in a similar way. Octafining (30) by Mobil is an example of an industrial method for producing
p-xylene. The boiling points for ethylbenzene, o-xylene, p-xylene, and m-xylene are 136°C, 143°C, 138°C, 138°C, respectively. From the C_8 aromatics, ethylbenzene is first removed as overhead in an ethylbenzene distillation tower. The bottoms are sent to a xylene splitter tower. There ortho-xylene and some C_8 compounds are removed as bottoms from the para- and meta-xylene. Downstream of that tower, the ortho-xylene is then recovered as overhead in another distillation tower. Separation of the overhead meta and para from the xylene splitter distillation tower is accomplished through fractional crystallization since para-xylene has a higher melting point (13.3°C) than meta-xylene (-47.9°C). After separation, the para deficient stream (mainly meta) is sent to an isomerizing reactor. After the light components are removed as overhead by a stripper, the remaining isomerization products are recycled to the xylene splitter distillation tower. The primary difference among the xylene isomerization patents lies in the choice of the catalyst.

Most researchers agree that xylene isomerization is an acid catalyzed reaction, with reversible steps. Several models have been put forward in literature, i.e. a series model (22,31-36),

\[ o \xrightarrow{m} p \]
a triangular model (37-39),

\[
\begin{array}{c}
\circ \\
\downarrow \\
\downarrow \\
m \\
\end{array}
\begin{array}{c}
\circ \\
\downarrow \\
\downarrow \\
p \\
\end{array}
\]

and a common intermediate model (40),

\[
\begin{array}{c}
\circ \\
\downarrow \\
\downarrow \\
1,2,4-\text{Trimethylbenzene} \\
\downarrow \\
m \\
\end{array}
\begin{array}{c}
\circ \\
\downarrow \\
\downarrow \\
p \\
\end{array}
\]

It should be apparent from the differences in these reaction schemes that the true mechanism has not been firmly established. There is, of course, the strong possibility that the mechanism may vary from one catalyst to another. A direct ortho to para conversion requires either a monomolecular 1,3-methyl shift or a bimolecular mechanism.

Generally, the evidence supporting the reported reaction schemes has been a better fit for the kinetic data. For example, arguments for a monomolecular mechanism in
HF-BF$_3$ mixtures have been the isomerization of the xylenes with no toluene production (41,42). Also, the lack of production of ortho- (or para-) xylene from para- (or ortho-) xylene at low conversion levels (31) over an amorphous silica-alumina catalyst implies a series mechanism.

A series mechanism requires only 1,2-methyl shifts since no direct ortho to para conversion is allowed. The existence of 1,2-methyl shifts was demonstrated by Roberts' (43) elegant study of $^{13}$C ring labeled toluene. The reaction of toluene-$1^{-13}$C treated with Al$_2$Br$_6$ and HBr in 1,2,4-trichlorobenzene solution at 35°C was investigated. Using mass spectrometry and NMR, he was able to monitor the movement of the methyl group relative to the labeled ring carbon. An increase in the ortho location followed by a decrease was seen. Also, a slow increase in the para and meta positions was seen. All these results can be explained by invoking only 1,2-shifts.

Direct evidence for a monomolecular 1,2-shift xylene isomerization mechanism over solid acids came from Corma and Cortes (31) using an amorphous nickel-loaded silica-alumina. At low conversions, no para-xylene was formed from ortho-xylene. This indicated a series mechanism. Then they isomerized a mixture of p-xylene labeled with deuterium in the methyl groups and non-labeled p-xylene. The products were analyzed using gc/ms. Very little hydrogen-deuterium scrambling occurred. Neither at low nor high conversions
did any of the xylene isomers contain mixed methyl groups. This implied an intramolecular isomerization mechanism. Thus, only 1,2-methyl shifts within a xylene molecule fit their results.

**Disproportionation**

An undesirable bimolecular reaction of two xylene molecules is disproportionation or transalkylation. Over all solid acid catalysts, this reversible reaction to toluene and trimethylbenzenes accompanies the isomerization of the xylenes, i.e.

\[ 2 \text{ Xylenes} \rightarrow \text{Toluene} + \text{Trimethylbenzenes (TMB)}. \]

The three TMB isomers are 1,2,3-, 1,3,5-, 1,2,4-trimethylbenzene. These are also known as hemellitene, mesitylene, and pseudocumene.

Collins et al. (33) indicated that isomerization was 2.9 times faster than disproportionation for ortho xylene over a LaY zeolite catalyst. However, for meta and para, that ratio was only 1.6-1.7. Thus, the reactivity of the isomer determined the amount of side reactions.

In electrophilic substitution, the ring positions ortho and para to a methyl group are activated due to its electron releasing effect. Based on this influence, a statistical substitution of methyl groups involving only the activated positions on the aromatic ring would result in the following values for the 1,2,3-TMB:1,2,4-TMB ratio: 1:1 for ortho-
xylene, 1:2 for meta-xylene, and 0:1 for para xylene. The
more stable 1,3,5-TMB is not expected from this reaction
scheme and would be formed only by secondary reactions.

The minimum cross-section molecular dimensions for
1,3,5-, 1,2,3-, and 1,2,4-trimethylbenzene are 8.6, 8.1, and
7.6 Å, respectively (44). Thus, the disparity in sizes in-
dicates a possibility that shape selective catalysts will
influence the product distributions.

Thermodynamics

Since the reactions are reversible, an accurate and
appropriate calculation of equilibrium constants is neces-
sary. Anselmo (45) cited reported cases of inconsistent
reaction rate coefficients for circular reaction schemes.
The laws of thermodynamics require that the product of the
equilibrium constants of a cyclical reaction scheme should
be unity. He stated that one way to ensure thermodynamically
consistent reaction rate coefficients is to assign
Gibbs free energies to the species.

Smith (46) presented a method for obtaining the equili-
brium concentration vector of a set of reactions by using
Gibbs free energies. The mass conservation equation for
each atomic element is

\[ \sum_{i} (n_{i}a_{i,k}) - A_{k} = 0, \quad (k=1,2,\ldots,w) \]  \hspace{1cm} (1)

where \( w \) is the number of elements in the system, \( n_{i} \) is the
number of moles of species $i$ at equilibrium, $a_{i,k}$ is the number of atoms of the $k$th element in compound $i$, and $A_k$ is the total number of atomic weights of the $k$th element in the system. The equilibrium constraint, derived from the minimization of the Gibbs free energy at equilibrium, is

$$\Delta G^0_{f,i} + RT \ln \left( \frac{n_i p_T}{\sum n_i} \right) + \sum_{k \lambda} \lambda_k a_{i,k} = 0, \ (i=1,2,...N) \quad (2)$$

where $N$ is the number of compounds in the system, $\Delta G^0_{f,i}$ is the standard free energy of formation for species $i$, $p_T$ is the total pressure in the system, and $\lambda_k$ is the Lagrange multiplier for element $k$. Equation 2) is valid for ideal gases. A set of $(N+w)$ linear equations results when mass conservation equations for the atomic elements are combined with equilibrium relations for each chemical species.

For this study, ideal behavior was assumed and the set of linear equations was solved by using a Levenberg-Marquardt algorithm, a standard least squares minimization routine. Data for the free energies of formation were obtained from reference (47). Equilibrium constants in this study were determined from the equilibrium concentration vector calculated by this method.
Isomerization Catalysts

A catalyst (probably an acid catalyst) is required to isomerize xylenes at moderate temperatures. Early work by Ward (48) and Crow et al. (49) established the lower temperature limit for thermal isomerization to be 550°C. Several types of isomerization catalysts have been used, including liquid phase, amorphous, and crystalline solids. Some examples of catalysts, reaction conditions, and postulated mechanisms follow.

Liquid Phase Catalysts

In the liquid phase, early catalysts were of the type HCl/AlCl₃ or HF/BF₃ (34,50). To prevent disproportionation, toluene was used as a diluent (51). Since it is a product of the transalkylation reaction, further production, by Le Chatelier's principle, would be inhibited by its presence. Roberts (52) reported a mechanism involving 1,2-methyl shifts for the liquid phase isomerization in trifluoromethanesulfonic acid. Using NMR, GLC, and conductimetric methods for the analysis of the reaction mixture, he found that the reaction was first order in the xylene reactant for xylene concentrations below 0.02 M. Above that concentration, the data appeared to follow second order kinetics, presumably due to the increased intimate ion pair formations between the xylenes and the catalyst. Similarly, Collins et al. (34) reported 1,2-shifts for the liquid phase isomerization in AlCl₃-HCl. They noted no para production
from ortho-xylene below 40% conversion. This indicated a series mechanism.

Liquid phase isomerization suffers from low reaction rates. Collins conducted his study at temperatures below 25 °C (34); Roberts conducted his at 25°C (43).

**Amorphous Silica-Alumina**

Separately, alumina and silica show no significant cracking activity (3). However, a chemical mixture of the two is quite active. Amorphous silica-alumina is made by co-precipitation of silica and alumina sols. The negative trivalent aluminum ion in tetrahedral coordination with four oxygen atoms must be balanced by a labile charge balancing cation, frequently Na⁺. This cation can be ion exchanged with NH₄⁺, which decomposes to H⁺ and NH₃ upon heating. The H⁺ bonds to an oxygen near an aluminum, thus balancing the negative charge and resulting in the formation of an -OH group. The NH₃ is thermally driven off the catalyst. This acid form, i.e. the H⁺ form, of the silica-alumina is catalytically active.

A vapor phase isomerization study over an amorphous silica-alumina, Houdry S-90, was conducted by Hanson and Engel (22). Since the reaction involved gaseous feeds, reaction temperatures were higher than for reactions carried out in the liquid phase. This resulted in faster reaction rates. These authors found that several undesirable side reactions accompanied the isomerization over this solid acid
catalyst. Most significantly, they noted a decrease in the isomerization activity with time caused by coking or fouling of the catalyst. After correcting all their kinetic data to a common value of activity, they were able to model the series reaction kinetics using a Hougén-Watson model for reversible adsorption with subsequent reaction on a single active site. Their activation energies for the conversion of meta to para and meta to ortho were 25.6 and 25.4 $\text{kcal mole}^{-1}$, respectively. Within experimental error, these are the same. They concluded that direct interconversion between ortho and para-xylene does not occur over S-90, indicating 1,2-methyl shifts.

Later work by Corma and Cortes (31,53) with silica-alumina loaded with Ni to minimize the activity decrease also led to the series mechanism with 1,2-methyl shifts (53). They found that the reaction was first order with respect to the xylenes and that the meta to para and meta to ortho activation energies were 22.8 and 22.3 $\text{kcal mole}^{-1}$, respectively. They speculated that since their activation energies were very similar to those calculated by Hanson and Engel, the role of the nickel loading was only to prevent coking. Similar activation energies were determined by Bhattacharya (35) for the series model over silica-alumina.

Zeolites

Zeolites have also been used for xylene isomerization. Zeolites are synthesized (4) hydrothermally at autogenous
pressures using a reactive silica source, e.g. silica sol or silicic acid, etc. and a reactive alumina source, e.g. sodium aluminate or hydrated alumina, etc. A difference between zeolite and amorphous crystallizations is the presence of a templating molecule in the zeolite synthesis. Usually a quaternary ammonium salt, the template forces the formation of micropores. As in the case of amorphous silica-alumina, the templating molecule behaves as a charge balancing cation and can be decomposed upon heating to produce Brønsted sites.

The main structural difference between these and amorphous silica-aluminas is that zeolites are three dimensional microporous crystalline structures. An advantage of the microporosity is that size discrimination is allowed among competing molecules, either reactants, intermediates, or products (54). Reactant selectivity implies that only certain molecules in a reactant mixture are of a shape and size suitable for admission into the catalyst pores. Product selectivity occurs when the products formed are too large to exit the pores and either block the catalyst sites or are subsequently cracked into smaller molecules which can leave the cages. Transition state, or intermediate, selectivity results from the prevention of the formation of a transition state due to its size. Weisz and Frilette (55) reported early evidence for reactant selectivity when they found that
n-butanol could be selectively dehydrated over a Linde Type 5A zeolite from a mixture of normal and iso-butanol.

The critical dimensions of the xylene isomers are: o-xylene, 7.6Å; meta-xylene, 7.6Å; and para-xylene, 7.0Å (56). Thus, it is possible to see a diffusional limitation of ortho and meta isomers over the para isomer if the pores are about the same size as the isomers.

Some molecular sieves and their pore dimensions are listed in Table 1. Unfortunately, most of the early work with xylene isomerization was conducted over large pore zeolites. Since the size of the pore openings was larger than the molecular dimensions of all the xylene molecules, no shape selectivity was possible. Lanewala and Boulton (40) concluded that the mechanism over a Lanthanum exchanged Y zeolite (LaY) involved a bimolecular reaction with a bulky trimethylbenzene intermediate. Similarly, Collins (33) reported a triangular model over a LaY catalyst. Gendy and Pratt (37) found that their data over HY zeolite also fit a triangular model. With these large pore zeolites, disproportionation competed with isomerization.

Over the small pore mordenite, a monomolecular series mechanism was found by Miklosy et al. (32). Using Langmuir Hinshelwood kinetics, activation energies of 36 and 34 kcal/mole for meta to para and meta to ortho were found. These values are higher than those reported for conversions over amorphous silica-alumina which were calculated from an Arrhenius
plot over a 45° temperature range. Carberry (57) stated that a sufficient temperature range is necessary to offset inaccuracies inherently present in the data. Satterfield (58) discussed the "false compensation" effect in activation energies resulting from error propagation. False compensation due to the small temperature range probably explains the slightly higher activation energies reported by Miklosy.

Over the natural zeolite ferrierite analog, Fu-9, Seddan (59) produced a concentration of p-xylene from m-xylene greater than thermodynamic equilibrium at low conversions. Since H-Fu-9 has ten-ring pore entrances, he postulated that the reaction pathways leading to a reduction of o-xylene were governed by stereo-control at the isomerization center, i.e. that the formation of o-xylene was blocked rather than its rapid isomerization to other products. He predicted a
1,2-methyl shift mechanism for xylene isomerization utilizing the transition state selectivity.

The zeolite catalyst used in largest volume for commercial xylene isomerization is ZSM-5. In 1980, it was used for about 60% of the western world's xylene isomerization. Developed by Mobil in 1972 (61), ZSM-5 possesses small pores with intersecting channels. One reason for its widespread use is that it has very low disproportionation activity (36, 38). After the exterior portion has been deactivated, the activity within the pores remains essentially constant. In fact, patents exist for the selective deactivation of the surface by polymer compounds, carbonaceous deposits, etc. (62-64). Low disproportionation activity is caused by the inability to form coke precursors inside the small ZSM-5 pores (65) due to transition state selectivity.

A description of the active sites on ZSM-5 was obtained by Babu (66, 67) by using temperature programmed desorption of NH\textsubscript{3}. From the presence of three peaks in the TPD at 373°C, 450-470°C, and 650-673°C, he concluded that three different types of hydroxyl groups exist on HZSM-5. These peaks were attributed to adsorption of the base on weak, medium, and strong acid sites. Interestingly, he found a linear relationship for the turnover number for o-xylene isomerization and the concentration of the strong acid sites. Haag (65) claimed that there is only one type of acid site on ZSM-5 and that additional desorption peaks
arise when excess ammonia is added. This would explain the lack of correlation between the turnover number and the weak and medium acid sites.

With the development of the highly active solid acid small pore ZSM series zeolites, some attention has again been focused on liquid phase isomerization. Mobil's Aromatics Processing (AP) process has reported a catalyst life of two years (68). The long life is probably due to solvation of the coke by the liquid reactants. Wise (69) presented a low temperature liquid phase isomerization process (LTI) utilizing ZSM-4 and no hydrogen pressure in the reactor. The LTI process could not convert ethylbenzene and an additional distillation column was necessary to remove it. Haag (25) presented an improvement to the LTI process by utilizing either ZSM-5, ZSM-12, or ZSM-21 to disproportionate ethylbenzene to benzene and diethylbenzene without affecting the xylenes. The operating conditions were similar to those used in the earlier LTI processes, i.e. 260°C, pressure sufficient to liquefy the reactant mixture, and no hydrogen.

**Coking**

Coking involves the deposition of hydrocarbon residues on the catalyst surface. McLellan et al. (70) studied the coke formation associated with methanol conversion over HZSM-5. They concluded that coke was formed initially at internal acid sites followed by external coke growth. All of their experiments were conducted at a single temperature,
370°C. Similarly, Langner (71) advanced the idea that coke precursors formed in the interior of the pores and then migrated out to the surface to form coke. Based on the reaction of propylene over NaNH₄Y, he postulated different mechanisms at different temperatures. Below 300°C, deactivation is initiated by coking inside the pores. Above that temperature, coking occurs at the entrances of the pores.

He based that statement on several observations. One was the rapid decrease of the pore volume of the catalyst to a nearly constant value at low temperatures, while at high temperatures the pore volume linearly decreased until it was zero. Also, the carbon/hydrogen ratio increased with temperature. Finally, ten times the amount of heptane soluble coke was found at lower temperatures than at high temperatures. All these pointed to the formation of dense complex structures at higher temperatures which formed on the exterior surface of the catalyst and slowly plugged the pore entrances. In fact, his chemical analysis of the high temperature heptane soluble coke indicated the presence of fused aromatics consisting of one to six rings.

Viner and Wojciechowski (72) studied the chemistry of catalytic poisoning and related it to the time on stream theory. By making a general model with concentration dependent deactivation, they concluded that there will be a "region of applicability" of the time on stream decay function.
As mentioned earlier, coking varies with the reaction temperature. It also varies with the reaction conditions. Gas phase reactions suffer from higher deactivation rates than liquid phase reactions. Gendy and Pratt (37) compared gas and liquid phase deactivations over HY zeolite. Using a time on stream correlation, they found that liquid phase reaction constants decreased 4-8 times more slowly than the corresponding gas phase reaction constants.

Recently, Corma (73) studied the effect of exchange level on coking. He prepared a series of rare earth exchanged Y zeolite samples with decreasing Na\(^+\) contents and increasing La\(^+\). With steamed catalysts, the amount of coke formation during n-heptane cracking decreased with respect to the non-steamed samples. He explained this result by postulating that the steam decreased the number and density of acid sites responsible for coking.

Obviously, coking influences the kinetics of a reaction. It is not sufficient to compare kinetic parameters on the same catalyst; one must also make sure that the data are collected at constant catalytic activity. Reported methods for obtaining kinetic data over coked catalysts are varied. One involves studying a catalyst that had been pre-coked and reached a constant level of activity (74). Another is to report the initial rate data (32) by extrapolating the data to zero time on stream. A third is to evaluate the rate constant's dependence on coking. This
involves either a time on stream study (22,37) or a constant coke level study (75). Thus, the kinetics of the reaction could be followed along with coking studies. All of these have the same objective, i.e. to report kinetic data independent of the coking level.
Active Sites

Description

One of the main research objectives in catalysis is to define the exact nature of the active sites. Since, for most zeolites, about 1% of the total available surface area is outside of the pores, the active sites are mainly in the cavities. Traditionally, the acidic activity has been associated with the aluminum (54). In the case of amorphous materials, the aluminum can exist in many forms (76). Uncertainty of the structure of aluminum has resulted in a controversy (77,78) over the nature of the active sites.

Inherently, in crystalline zeolites, the placement and surrounding structure of the aluminum is more precisely defined. ZSM-5 offers a unique opportunity to study zeolite catalysts because of its low and controlled aluminum content. Over ZSM-5, the active site count for hexane cracking was found (65) to correspond with the number of aluminum atoms. The relative rate constant for catalytic cracking is proportional to the aluminum content over about four orders of magnitude. Additionally, the cracking activity varies linearly with the intensity of an NMR signal due to tetrahedral Al (65). The absence of Lewis-bound pyridine (79) also indicates that the aluminum is in tetrahedral coordination. Since Al is in tetrahedral, rather than triangular, coordination all these findings seem to indicate
that the active sites are Brønsted, rather than Lewis, in nature.

With these thoughts in mind, the following are the active sites as postulated by Gates (3) and Satterfield (58). For amorphous silica-alumina, the structure of the active sites, \( \text{H}^+ \) 's, is thought to be

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} & \quad \text{H} & \quad \text{O} \\
\text{O-Si-O-Al-O-Si-O} & 
\end{align*}
\]

The OH groups terminating the primary silica and alumina particles vary from weakly acidic to alcoholic and show very little Brønsted activity. However, the \( \text{H}^+ \) ions associated with the co-gelled mixed oxide possess significant acidic character. Heating to high temperatures causes the removal of \( \text{H}_2\text{O} \) from the Al and the formation of a Lewis acid with a resulting decrease in Brønsted sites.

Since the structure of amorphous silica-alumina is not known, there may exist aluminum structural arrangements other than that listed above which contribute to active sites. In fact, Peri (76) has proposed five different structures. Each has a different type of bonding surrounding an aluminum atom. This in turn suggests that each site will have specific characteristics of acid strength, steric surroundings, etc. which will influence its activity as an acid site.
For zeolites, the Brønsted sites, H\(^+\)s, are

\[
\begin{array}{c}
\text{H}^+ \\
\text{O} \quad \text{Si} \quad \text{O} \quad \text{Al} \quad \text{O} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{array}
\]

It has been observed that the number of Brønsted sites decreases upon heating to temperatures higher than 450°C. Hall and Uytterhoeven (80) proposed the following dehydroxylation mechanism, where the structure above loses a water molecule, viz.

\[
\begin{array}{c}
\text{O} \quad \text{Si} \quad \text{Al} \quad \text{Si} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{array} + \text{H}_2\text{O}
\]

Thus, two Brønsted sites convert to one Lewis site. Using base adsorption and IR techniques to quantify the relative amounts of each, Ward (81) and Jacobs et al. (82) demonstrated the two-to-one relationship over HY and NH\(_4\)Y zeolites, respectively.

**Quantification**

The formation of Lewis sites on zeolites can be minimized by keeping the pretreatment temperature below 500°C. Several methods exist for counting the number of acid sites on the surface of the solid acid. Benesi and Winguist (83) and Vedrine et al. (84) mention most of the available methods. Among those discussed are indicator
methods, adsorption of gaseous bases, infrared spectroscopy, and chemical titration with model reactions.

Anderson and Klinowski (86) presented a method for determining acidities of zeolites through the use of indicators. Their method involves anhydrous benzene as diluent, n-butylamine as the titrating base in an ultrasonic bath, and a UV spectrophotometer to detect the color change at the endpoint. They cautioned against the use of certain indicator molecules, such as anthraquinone, for the zeolite acidity measurements since their size would prevent them from entering the micropores.

Adsorption of gaseous bases is not selective. Usually these experiments are performed at temperatures lower than the actual reaction temperature (82). As a result, non-selective physical adsorption at the lower temperatures on the surface will mask the chemisorption of the bases on the acid sites. The basic molecules will adsorb on sites under experimental conditions where they would not adsorb under reaction conditions. This would contribute to an overestimation of the actual catalytic site count. Thus, a direct calculation of the amount of base adsorbed on the acid sites is not possible. For example, Jacobs et al. (82) calculated the number of hydroxyl groups from NH₃ adsorption experiments at room temperature. They found that the initial cumene dealkylation activity after different pretreatments (at temperatures between 500° and 800°C)
decreased much more slowly than the concentration of acidic hydroxyls. He concluded that only a fraction of the hydroxyls are involved in the reaction, which is a reasonable conclusion based on the preceding statements.

The best method for acid site count and strength is a combination of IR and microbalance techniques. The weight of the base adsorbed on the catalyst after heating to remove physically adsorbed molecules leads to an upper value for the absolute number of sites. The relative number of Lewis and Brønsted sites can be found from IR transmission bands due to the different coordinations of the basic molecule over the two acid sites. However, the method loses sensitivity if the sample must be cooled after base introduction and before IR analysis, as is often the case (81,87-89). Schwarz (90) reports a physical integration of the two techniques to give in-situ IR measurements and remove the previous handicap. However, he also reported that the technique for gaseous base introduction must be qualified by stipulating the type of titer used since weak acid sites will not adsorb the gaseous base.

Chemical titrations have been performed to characterize the acid sites by Turkevich (91). A model reaction is run on a catalyst by alternating pulses of reactant and poison. After conversion drops to zero, the titer is the cumulative amount of poison injected. However, loss of the base through continual bleeding cannot be ruled out of this method.
Another model reaction referred to by Benesi and Winquist is hydrogen-deuterium exchange in hydrocarbons. The idea is that there is a one-to-one correspondence between the hydrogens exchanged and Brønsted sites. However, they mention that this method will give anomalous behavior under certain situations since the reaction is facile, i.e. it can occur over metals or strong bases.

Table 2 lists a comparison of several of the methods. It was adapted from Gates (3) and contains a listing of the Brønsted site densities of HY zeolite. Additionally, values are listed for the theoretical densities calculated from the aluminum content.

Table 2

<table>
<thead>
<tr>
<th>Method of Acidity Determination</th>
<th>$10^{-21} \times$ number of OH Groups per gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural</td>
<td></td>
</tr>
<tr>
<td>Total H</td>
<td>2.9</td>
</tr>
<tr>
<td>H Protruding into Supercage</td>
<td>1.4</td>
</tr>
<tr>
<td>Titration with n-Butylamine</td>
<td>1.3</td>
</tr>
<tr>
<td>Poisoning of Cumene Cracking Activity</td>
<td>1.0</td>
</tr>
<tr>
<td>Deuterium Exchange with Benzene</td>
<td>0.9-1.2</td>
</tr>
</tbody>
</table>

$^1$ SiO$_2$/Al$_2$O$_3$ ratio was 5.0
All these methods led to approximately the same result. Interestingly, the site density calculated from the hydrogens protruding into the supercage is closer to the values reported by the other methods than the total hydrogen content. As mentioned earlier, the sites in the sodalite unit are inaccessible to most molecules and would not be counted by the methods listed.

Catalyst Structures

The structures considered in this study provide for a variety of isomerization conditions. There is a large-pore molecular sieve with appreciable catalytic activity, HSAPO-5; a large-pore molecular sieve with low catalytic activity, HAlPO-5; a medium-pore zeolite, HZSM-5; and an amorphous solid acid catalyst, Houdry M-46. When the catalysts are examined under the same conditions, a general determination of the xylene isomerization mechanism, or specific parts of it, may be possible.

AlPO-5

Wilson et al. (94) have reported that AlPO-5 has a microporous three dimensional framework structure with hexagonal symmetry. The unit cell composition is $\text{Al}_2\text{O}_3:1.0\pm0.2 \ P_2\text{O}_5$. AlPO-5 contains one-dimensional channels oriented parallel to the c axis and bounded by twelve alternating $\text{AlO}_4^-$ and $\text{PO}_4^+$ tetrahedral units. The "free" channel
cross-section dimension is 8 Å. This structure is shared by SAPO-5.

**SAPO-5**

SAPO-5 has a microporous tetrahedral oxide framework containing silicon, aluminum, and phosphorous. It has hexagonal symmetry. A typical empirical formula for the catalyst is \( mR: (Si_xAl_yP_z)O_2 \), where \( R \) represents at least one templating agent present in the intracrystalline pore system. Generally, \( m \) has a value from 0.02 to 0.3 (13). It contains one-dimensional channels parallel to the c-axis. As in AlPO-5, both the pore entrance and the interior of the pores are bounded by twelve tetrahedral units.

Lok et al. (92) suggested that SAPO's are formed by silicon substitution into the aluminophosphate network. They proposed that three substitution mechanisms could occur: 1) silicon substitution for aluminum, 2) silicon substitution for phosphorous, or 3) simultaneous substitution of two silicons for one aluminum and one phosphorous. He suggested that the substitution occurs through the second and third mechanisms, although no experimental evidence was presented. Appleyard et al. (93) provided evidence for involvement of the second and third mechanisms by using multinuclear Magic Angle Spinning (MAS) NMR. His experimental chemical shifts and linewidths were consistent with previous studies on AlPO-5, proving that the basic structure of SAPO-5 is alternating \( AlO_4^- \) and \( PO_4^+ \) tetrahedra.
ZSM-5

Kokotailo et al. (95) reported that ZSM-5 consists of a novel configuration of linked AlO$_4^-$ and SiO$_4$ tetrahedra. With orthorhombic symmetry, the composition of the unit cell is Na$_n$Al$_n$Si$_{96-n}$O$_{192}$$\cdot$16H$_2$O, where n<27 and typically 3 (61). Contributing to the microporosity are two intersecting channel systems. One system is sinusoidal and the other consists of straight channels parallel to each other as indicated in Table 1 (pg. 21). The entrances to the pores are formed by ten tetrahedral units. The "free" channel cross-section dimensions are 5.4Å for the nearly circular cross-sectioned zig-zag channels and 5.8 X 5.1Å for the elliptical cross-sectioned straight channels (96). This structure is very similar to that of silicalite (97), a microporous three dimensional structure developed by Union Carbide that is essentially pure silica.

Amorphous Silica-Alumina

The silica-alumina used in the study was a commercial Houdry catalyst, M-46. The catalyst was amorphous to x-ray diffraction. It was composed of 12.5 wt% alumina and had Fe at a level of 0.1 to 0.3 wt.% as the major impurity (98).
II. Experimental

Catalysts

The HSAP0-5 form of the catalyst was obtained from the crystallized sample (vide infra p. 53) by calcination in air at 500°C. This caused the decomposition of the templating molecule, triethylamine. After calcination, the resulting powder was pelletized, crushed, and sieved to 30-50 mesh particles. Since the Ludox AS-40 form of silica sol was used in the preparation, no cation exchange was necessary to achieve the hydrogen form. Ludox AS-40 silica sol is the ammonium stabilized form, i.e. sodium-free.

A comparative study was made with three other catalysts. They were AlPO-5, ZSM-5, and Houdry M-46 silica alumina. Their physical properties are reported later with SAPO-5's. The AlPO-5 was donated by Union Carbide. ZSM-5 was donated by Mobil. A small sample of the M-46 catalyst was obtained from the Houdry Division of Air Products and Chemicals, Inc. No special pretreatment such as calcination to remove templating molecules was necessary since they were in their final catalytic form.
Chemicals and Gases

For the kinetic experiments, the following chemicals and gases were used

- ortho-xylene, 97% by weight
- para xylene, 99% by weight
- meta-xylene, 99% by weight
- Catapal alumina
- Phosphoric acid, 85% by weight
- Ludox AS-40 silica sol, 40% by weight
- Helium grade 4.5
- Hydrogen, grade 4.5
- Oxygen, grade 4.3
- Compressed air, breathing air grade
- Carbon dioxide, grade 4.0

All of the gases were obtained from Magnolia Welding Supply. The xylenes were obtained from Aldrich Chemicals. Alumina and silica sol were kindly donated by the Vista Chemical Company and the E. I. du Pont Company, respectively. The phosphoric acid (reagent grade) was obtained from Baker.

Labeled ortho-xylene-$\alpha,\alpha'$-$^{13}\text{C}_2$ was purchased from Merck, Sharp, and Dohme with an isotopic purity of 99.5%. Deuterium labeled ortho-xylene was purchased from Aldrich with an isotopic purity of 99.7%.
Apparatus

Crystalization Chamber

Figure 3 illustrates the vessel used for the synthesis of the SAPO-5 catalyst. The 320 ml chamber was designed for use in hydrothermal crystallizations at autogenous pressures. The design incorporates a relief valve for safety reasons. Pressures in the range of 200 psig were observed during early runs. Consequently, a relief valve rated at 750 psig was used for all subsequent crystallizations. The stainless steel outer shell provided the strength necessary to withstand the autogenous pressures. The teflon inner jacket ensured that the steel walls would not influence the synthesis of the catalyst since the crystallization was performed in a corrosive media. Although the maximum feed volume possible is 320 ml, the amount of product that can be prepared depends on many things, including crystallization temperature, time, etc.

Flow Reaction System

The reaction system used in this study was adapted from one used by Machiels et al. (99). On Figure 4, inlet purifiers were used to maintain clean helium to the reaction system and the gas chromatograph and clean compressed air to the FID detector by removing trace hydrocarbons and water. Inlet regulators maintained the same constant upstream
SYSTEM Plumbing

Figure 4
pressure necessary to ensure proper mixing of several feed streams.

In the inlet portion of the system (Figure 5), three Tylan mass flow controllers, Model PC 260, monitored the feed gases. They were calibrated for helium, oxygen, and butane. Calibration to other gases was possible through the use of a conversion constant. For example, a conversion constant was used when the flow of carbon dioxide was monitored by the flow controller calibrated for butane. The Tylan PS-14 power supply and RO-14 readout allowed for adjustment of feed gas flow setpoint. The line leading to the injector (the Inlet Line) was heated by a heating tape to 82°C. A Harvard pump drove a microliter syringe filled with the liquid feed reactants into the feed stream. The injector was salvaged from a Perkin-Elmer 3920 gas chromatograph. It was kept at 212 °C by a combination of rod heater and Variac. The resulting drops from the syringe were smoothed out by the 100 cc mixing volume, a glass vessel connected to the system with two glass-to-metal joints. The mixing volume was kept at 350°C by a Variac powered Electrothermal heating mantle. The lines around the mixing volume and its bypass were heated by a heating tape to 100°C.

In the reaction portion of the system (Figure 6), a Series 300 Antek oven maintained the recirculation portion of the reactor at 110°C. A Metal Bellows MB41HT pump maintained a continuous recirculation flow through the
Figure 5
Figure 6

REACTOR Plumbing

Recirculation Oven

Recirculation Pump

RV1

RV2

RV3

RV4

Reactor Resistance Heater

Reactor

Omega 640 Recorder

Leads and Northrup Temperature Controller
reactor. At a system pressure of 2 psig, the flow was 4500 cc(stp)/min. A Leeds and Northrup Electromax V Plus temperature controller maintained the reaction temperature by supplying power to the resistance heater surrounding the reactor. The temperature was controlled by monitoring the thermocouple inside the heater and outside of the reactor. A coaxial thermocouple monitored the actual reaction temperature and displayed it on one channel of a dual channel Omega Model 640 Strip Chart Recorder. Bypassing the reactor was possible through the use of the three-way valves, RV3 and RV4. The valve RV2 was used to maintain a pressure drop across the pump equal to the reactor pressure drop when bypassing the reactor during startup.

In the analysis portion of the system (Figure 7), an on-line Valco ten-port valve, AV-1, was used to sample the reaction mixture. Two detectors monitored the peaks. The FID detector was used for the analysis of reaction compounds. The TCD detector was used to analyze regeneration run peaks, usually O₂ and CO₂. When used to analyze the regeneration gas, the TC detector was brought on stream by turning the four-way valve AV4. Both detectors were operated in their linear regions, as can be seen in Tables 19 and 20 in Appendix F. The reaction compounds were separated on a 1/8 inch o.d. stainless steel column, 24 feet long. The column packing was 5% AT-1200+5% Bentone-34 on Chromosorb X, 80-100 mesh. A second 6 feet 1/8 inch stain-
less steel column filled with Porapak N was used to separate the regeneration products. A Hewlett Packard 3390A integrator reported the chromatogram and areas of the eluting peaks. A "homemade" thermal conductivity detector monitored the overall flow during the experiments. Its output was sent to the second channel of the Omega recorder. The TCD was maintained at 185°C by a heating tape and Variac. Finally, a cord heater and Variac maintained the system lines at temperatures high enough to prevent condensation, i.e. 80-100°C.

The operation of the ten-port valve, AV-1, is illustrated in Figure 8. In Position A, analysis of the reaction products was performed. Also, in this position the sample loop for the regeneration products was filled. In Position B, the regeneration products were analyzed. While in this position, the sample loop for the reaction products was filled. With this alternate, 2-loop, 2-detector operation, samples were admitted to the columns that were not being integrated. The only problem that arose from this setup was that an initial treatment of the columns was necessary.

Flow tracer experiments were used to verify that the system behaved as a continuous stirred tank reactor, CSTR. In Figure 46 in Appendix A, the typical CSTR responses from the reaction system to impulse and step inputs are seen. Note the different time scales for the two responses. The spikes in the step response were due to the on-line sampling
Valve AV-1:
Gas Sample with Alternate 2-Loop,
2-Column, 2-Detector Operation

Figure 8
with AV-1. These minor flow fluctuations were caused by the exposure of the higher pressure in the sample loop from the gas chromatograph to the reaction system when AV-1 is turned to Position B.

**Microcatalytic Pulse System**

Microcatalytic pulse experiments were carried out in the dual pass arrangement illustrated on Figure 9. This arrangement was adapted from one described by Galeski and Hightower (100). The reactor bed was a Cajon stainless steel VCR double male union. The sample trap was necessary since partial separation of the reaction mixture occurred in the catalyst bed. Valves MV2 and MV3 were switched in sequence from one position bypassing the sample trap to another admitting the sample into the gas chromatograph. Valve MV1 was used to isolate the sample trap from the reaction lines.

The same column used in the kinetic experiments was employed here. However, a temperature program was run to optimize the separation. Starting at 80°C, the oven was immediately heated to 120°C at 4 °C/min and maintained at that temperature until all peaks had eluted.

Again, the TCD was a "homemade" detector. Samples for use in the mass spectrometer were collected with the trap on the outlet line of the TCD. All the lines in the microcatalytic pulse system were heated to prevent condensation of the reactants.
Microcatalytic Pulse Reactor System
Dual Stream Arrangement

(All lines heated)

Figure 9
Mass Spectrometer

The analysis of the stable isotopes in both the deuterium scrambling and $^{13}$C studies was conducted on a Consolidated Electrodynamics Corporation 21-104 mass spectrometer. The inlet system consists of a three liter sample volume equipped with an MKS Baratron Pressure Gauge. A valve was inserted downstream of the sample volume to allow its isolation from the inlet system. Vacuum in the inlet system was maintained by an oil diffusion pump and forepump combination. There was an additional diffusion-fore pump combination for startup of the mass spectrometer. Normally, an 80 liter/sec Varion VacIon pump maintained a vacuum in the analyzer chamber. The gas samples were admitted into the analyzer section through a gold foil leak. During all experiments an ionizing voltage of 6.5 Volts nominal and a slit width of 0.15 mm were used. No detectable fragmentation was seen at these settings.

BET Apparatus

All surface area and pore volume studies were conducted on a Micromeritics Accusorb analyzer. An internal oil diffusion pump and forepump combination allowed vacuum outgassing of the samples at elevated temperatures maintained by sample mantle heaters powered by Variacs. A manifold allowed for the introduction of nitrogen into the samples at
liquid nitrogen temperature. After pressure equilibration, the pressure was read from an electronic pressure gauge.

**Neutron Activation**

Both of the thermal and fast neutron activation studies were conducted by the Center for Trace Characterization at Texas A&M University. A KAMAN Sciences sealed-tube neutron generator Model 17-10 capable of generating $10^{11} \text{neutrons} \frac{1}{\text{cm sec}}$ at 14.7 MeV was used during the fast neutron experiments. The thermal neutron experiments were performed with a General Atomic TRIGA Research Reactor which generated $10^{13} \text{neutrons} \frac{1}{\text{cm sec}}$ at 0.025 MeV.

The Gamma rays produced were detected by a Ge(Li) solid state detector connected to with a Nuclear Data Multichannel Analyzer Model ND-66. The analyzer was interfaced to a PDP-11/24 minicomputer.

**Atomic Adsorption**

Elemental analysis of the silicoaluminophosphate with this method was done at Mobil's Paulsboro Laboratory.
X-ray Analysis

Two independent studies of the crystalline structure were carried out on the crystallized samples. The first study was conducted to make sure that the sample had indeed crystallized. The second was performed to generate quantitative data about the intensities of the x-ray diffraction peaks.

Guinier-Haegg Camera

Located in the Chemistry Department, a copper x-ray generator produced the necessary radiation for the x-ray analysis. The generator was set at 36 kilovolts and 18 milliamps. The x-ray experimental data were recorded on a thin section of x-ray film. The d-spacings were calculated by a program of the Bragg equation on a PDP 11/70 minicomputer using distance measurements taken from the film. Very little information of the intensities of the peaks could be derived by this method.

X-ray Powder Diffraction

X-ray powder diffractograms were run at Shell's Westhollow Lab. The generator settings were at 45 kilovolts and 35 milliamps. The step size and count time were 0.02 degrees and 0.30 sec, respectively. Intensity data were plotted versus 20.
Experimental Procedure

Crystallizations

Although the amount of crystallized product depends on the temperature, pressure, etc. applied to the preparation vessel, those variables were not studied for this work, in which only one sample of SAPO-5 was required. A known procedure (Union Carbide, USP 4,440,871 (14)) which results in a high yield of product was followed. The only modification was to scale up the procedure so that a larger batch of catalyst could be made.

In a 500 ml glass beaker, the following were mixed together:

- 105.4 ml H₂O (distilled and de-ionized)
- 34.1 ml H₃PO₄, 85wt%

When the mixture cooled to room temperature, 34.8 grams of Catapal alumina (74.2wt%) were added slowly under stirring. When a homogeneous gel was seen, 75.5 ml of Ludox AS-40 (40wt%) were slowly added. Again, stirring homogenized the mixture. Finally, 71.0 ml of triethylamine (Et₃N) were added as a templating agent.

After stirring produced a homogeneous mixture, the reactants were poured into the crystallization chamber. The final mix resulted in the composition (molar basis)

\[1.2\text{Et}_3\text{N}:0.03\text{Na}_2\text{O}: (\text{Si}_{0.4}\text{Al}_{0.3}\text{P}_{0.3})\text{O}_{10.9}\text{H}_2\text{O}\.

The chamber was heated to 200°C for 160 hours.
After it cooled to room temperature, de-ionized water was added to help remove the solids from the crystallization chamber. The contents of the chamber were filtered and washed with water. After drying in air, the solids were heated in an oven at 100°C until visibly dry. Although this step did not remove the templating molecule, it did remove the water left over from the crystallizations and washings.

Kinetic Experiments

The stainless steel fittings compromising the reactor were unassembled and the catalyst particles were placed inside the reactor bed between two glass wool plugs. To prevent the joints from siezing at the high reaction temperatures, a commercial anti-sieze agent was applied over the threads. After the reactor was assembled, the resistance heater was raised around it.

These experiments were initiated by flowing helium through the system to remove all traces of air. Both the mixing volume and its bypass were flushed with helium. Control of the helium flow was accomplished with the Tylan flow controller and kept at a higher flow than during the experiments. The heaters to the reaction system lines were turned on, as were the heating mantle for the mixing volume, the injector, and the recirculation oven. The heater for the outlet TCD, as well as the gas chromatograph, remained on continuously.
The catalyst bed was heated to the reaction temperature by raising the setpoint on the Leeds and Northrup temperature controller. Helium flow was lowered to experimental conditions during this time. When the temperature was reached, the reactor was bypassed by turning valves RV3 and RV4. With the feed syringe inserted into the injector septum, gears on the Harvard microliter syringe pump were adjusted to deliver the desired flowrate.

When the mass flowrate of the feed stabilized, as monitored by the outlet TCD, the reactor was brought on-stream by turning valves RV3 and RV4 simultaneously. After the flow stabilized again, samples were taken by turning valve AV1.

Since the catalytic activity decreases as the catalyst ages (see p. 87), reporting kinetic data requires a description of the catalyst at the reaction conditions. The method chosen to obtain data at constant catalytic activity was to report data at the initial time on stream. Thus, initial data experiments normally lasted four hours. Deactivation runs were longer.

**Regeneration**

Regeneration of the catalyst was accomplished by flowing helium and oxygen over the catalyst bed immediately after a kinetic run at the conditions stated in Note 1 of Table 7. This same procedure was followed for a fresh catalyst. Unnecessary delays in the startup of the next
kinetic experiment were avoided by bypassing the mixing volume. The Tylan mass flow controllers for O₂ and helium were used to control the flow of the gases. All heaters were left on. Helium was necessary as a diluent to prevent high temperatures from forming on the catalyst during the exothermic coke oxidation reactions. The Porapak N column was used to quantify the amount of CO₂ produced. As in the kinetic experiments, sampling was accomplished through Valve AV1. Also, in order to use the outlet TCD as the detector during the regenerations, the four-way valve, AV4, was rotated to allow the line downstream of the Porapak N column to flow into the detector and vent the system line.

Microcatalytic Pulse System

Deuterium Exchange

Three types of exchange experiments were conducted. They involved passing pulses of different reactants over catalysts that had been subjected to different pretreatments. D₆-benzene was passed over the surface covered with hydrogen only. A mixture of o-xylene and d₁₀-o-xylene was passed over a surface covered with equal numbers of hydrogens and deuteriums. Finally, a mixture of cumene and d₆-benzene was passed over a catalyst surface covered with deuteriums only.

Benzene

The apparatus used to carry out the deuterium exchange reactions is illustrated in Figure 9. With all the system
lines heated, the microcatalytic reactor was heated to a reaction temperature in the range of 350 to 450°C. The helium flow through the system was chosen to be similar to the experimental flow into the CSTR system. Two μliter pulses of reactants were injected upstream of the reactor, and the products were collected in a trap located in the vent side of valve MVI by condensing with liquid nitrogen.

Initially, d₆-benzene was passed over the catalyst covered only with H atoms. No chromatographic separations were necessary since benzene did not form other compounds over any of the catalysts. Usually, six pulses of d₆-benzene were injected. For one sample, AlPO-5, fourteen pulses were made since there was very little exchange per pulse.

Analysis of the deuterated isomers was conducted by admitting the samples to the CEC mass spectrometer. The trap was kept at liquid nitrogen temperatures while evacuating with the inlet vacuum system to remove helium and other non-condensable gases.

After the d₆-benzene pulses were trapped and analyzed, d₀-benzene pulses were passed over the same catalyst to ascertain the deuterium recovery efficiency.

**Ortho-Xylene**

The same method for trapping and analyzing the benzene exchange products was applied when o-xylene was the reactant. The catalyst was pretreated with a d₀:d₆-benzene
mixture (50:50, molar) to equilibrate the surface with equal numbers of H's and D's. Then, 2 μliter pulses of a feed mixture composed of 50% \( \text{d}_0 \)-o-xylene and 50% \( \text{d}_{10} \)-o-xylene were passed over the catalyst at different reactor temperatures and carrier flowrates.

**Cumene and \( \text{d}_6 \)-Benzene**

The catalyst was pretreated with five pulses of \( \text{d}_6 \)-benzene to cover the surface with D atoms. Analysis of the gas phase indicated that no more exchange occurred after that number of pulses. The feed mixture consisted of cumene and \( \text{d}_6 \)-benzene in a molar ratio that would result in a 10:1 deuterium to hydrogen ratio in the gas phase. In this case, a chromatographic separation was required to separate benzene and cumene. Also, a special vacuum grease-free trap was required since cumene adsorbed rather easily on the grease due to its high boiling point.

\( 13 \text{C} \) Tracers

The same injection and trapping procedure for the deuterium exchange reactions was followed for this study. However, the feed was a mixture of \( 13 \text{C} \) and non-\( 13 \text{C} \) labeled ortho-xylene. Again a constant temperature was used in the reactor. Since a chemical reaction occurred, chromatographic separation of the products was necessary. Usually, the product was trapped in the trap downstream of the "homemade" TCD. An important difference in this study was
that the number of isomers was three. In the deuterium studies, the isomers totaled eleven. Also, since the conversions were kept low to minimize side reactions during these experiments, the three liter feed volume was not used. This was accomplished by closing the valve to the feed volume.

X-ray Analysis

Guinier-Haegg Camera

In order to photograph the x-ray diffraction spectra, the camera on the apparatus was removed. In a dark room, a thin rectangular section of x-ray film was loaded into the outer circumference. With the shutter closed, the camera was moved to the x-ray source. A thin layer of the sample, in powder form, was placed on a plate. The x-ray apparatus was turned on. The lowest generator settings were set. With the plate rotating and the shutter released, an exposure of a reference line was taken. The generator was then adjusted to its operating levels and an exposure was initiated. Normally, four hours were allotted for the exposure to the catalyst samples.

Upon completion of the exposure, the camera was again taken into the dark room where the film was removed and placed in a developing tank. The film was developed by contacting it successively with developing liquid, stop liquid, and fixing liquid. Finally, the film was washed with water before being removed form the developing tank.
X-ray Powder Diffractometer

X-ray powder diffraction experiments resulting in intensity data were all performed by Shell's Westhollow Labs.

Treatment of Data

Kinetic Experiments

Typical data recorded during a kinetic run were catalyst weight, feed composition, reaction temperature, carrier flowrate, volume of feed syringe, syringe pump gear, and areas of the eluting peaks. The areas were recorded from the response of the FID detector. The feed composition, the volume of the feed syringe, and the syringe pump gear were used to calculate the molar flowrate of the feed. Appropriate calibration factors were used to convert the areas to either weight fractions or mole fractions. Implicit in the previous calculations were the two assumptions: no volume change during reaction and a mass balance around the reactor. Since the reactants contributed a very small amount to the total flowrate (∼3 mol%), the changes due to the reaction were negligible. Also, the overall flowrate was monitored by the "homemade" TCD. During the kinetic runs, the variation of the overall flowrate was within ±4%. Thus, the assumption of a mass balance was a reasonable one.

For initial rate data experiments conducted over four hours, the objective was to obtain the conversion at zero time on stream. Following the time on stream theory, the
data were plotted on a semilog axis and extrapolated to zero time on stream.

Regeneration

Data recorded during a regeneration run were the areas of oxygen and carbon dioxide, flowrates of helium and oxygen, and the reaction temperature. The areas recorded from the TCD response were converted to mole fractions. Multiplication of the CO$_2$ mole fraction by the total flowrate led to the volumetric flowrate of CO$_2$ as a function of time. Integrating the volume of CO$_2$ led to the grams of carbon on the catalyst. The weight percent of carbon was referred to as weight percent of coke.

Microcatalytic Pulse System

Deuterium Exchange

The same procedure was followed for analyzing the data from the benzene, ortho-xylene, and cumene experiments. Raw data collected included the mass spectra of deuterated isomers traced on the mass spectrometer strip chart recorder. The tabulated peak heights were corrected for $^{13}$C impurities. The number of H atoms on the surface was then calculated from the distribution of deuteriums in the isomers. Appendix E describes the calculation procedure.
$^{13}$C Tracers

Raw data collected during this study were the mass spectra of the separated isomers in the products. The mass spectral peaks were corrected for $^{13}$C impurities. Corrections for fragmentation were not necessary since fragmentation was negligibly small.

X-ray Analysis

Guinier-Haegg Camera

Data recorded from the camera experiments were the diffraction line spectra from the film. Physical measurements were taken from the film. Linear measurements from the reference line to all observable lines were recorded. Only diffraction lines were measured. Care was taken to avoid using reflection lines. These were converted to d-spacings with a program on a supporting PDP 11/70 minicomputer.
III. Results

Catalyst Structure and Composition

Elemental Analysis

Neutron activation and atomic adsorption studies were conducted on HSAPO-5. While the former method was sensitive to aluminum, it led to only relative values between silicon and phosphorous. The latter method was required to determine the silicon and phosphorous composition.

The two reactions used to determine the aluminum content were

\[ ^{27}\text{Al}(n,p) \rightarrow ^{27}\text{Mg} \quad (3) \]
\[ ^{27}\text{Al}(n,\gamma) \rightarrow ^{28}\text{Al} \quad (4) \]

Both fast (eq. 3) and thermal (eq. 4) neutron activation studies indicated that HSAPO-5 consisted of 21.2 weight% aluminum. However, the following reactions overlapped when analyzed with fast neutrons

\[ ^{27}\text{Si}(n,p) \rightarrow ^{28}_{13}\text{Al} \quad (5) \]
\[ ^{31}\text{P}(n,a) \rightarrow ^{28}_{13}\text{Al} \quad (6) \]

Through the use of atomic adsorption, the silicon and phosphorous contents were found to be 4.0 and 14.5 weight%, respectively. Thus, with the combination of the two methods, the empirical formula (mole fraction including Al, Si, and P only) for HSAPO-5 was found to be

63
(Si$_{0.10}$Al$_{0.56}$P$_{0.34}$)O$_2$.

X-ray Diffraction

After each run, in order to confirm that the solids in the crystallization chamber were indeed crystalline, an x-ray diffraction pattern of each sample was taken with a Guinier-Haegg camera. Only samples that evidenced x-ray diffraction lines on the film were studied further by an x-ray diffractometer.

The analysis of virgin HSAPO-5 resulted in the d-spacings listed in Table 3. Also listed there are the d-spacings from the HALPO-5 and HSAPO-5 Union Carbide patents (11,14).

Table 3
Comparison of D-Spacings, Å

<table>
<thead>
<tr>
<th>Virgin HSAPO-5</th>
<th>Patents</th>
<th>Virgin HSAPO-5</th>
<th>Patents</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.9</td>
<td>11.8</td>
<td>11.8</td>
<td>11.8</td>
</tr>
<tr>
<td>6.8</td>
<td>6.84</td>
<td>6.84</td>
<td>6.84</td>
</tr>
<tr>
<td>5.9</td>
<td>5.91</td>
<td>5.93</td>
<td>5.93</td>
</tr>
<tr>
<td>4.5</td>
<td>4.46</td>
<td>4.50</td>
<td>4.50</td>
</tr>
<tr>
<td>4.2</td>
<td>4.24</td>
<td>4.24</td>
<td>4.24</td>
</tr>
<tr>
<td>3.97</td>
<td>3.95</td>
<td>3.97</td>
<td>3.97</td>
</tr>
<tr>
<td>3.61</td>
<td>3.60</td>
<td>3.61</td>
<td>3.61</td>
</tr>
<tr>
<td>3.4</td>
<td>3.40</td>
<td>3.43</td>
<td>3.43</td>
</tr>
<tr>
<td>3.08</td>
<td>3.09</td>
<td>3.08</td>
<td>3.08</td>
</tr>
<tr>
<td>2.97</td>
<td>2.95</td>
<td>2.97</td>
<td>2.97</td>
</tr>
<tr>
<td>2.66</td>
<td>2.66</td>
<td>2.67</td>
<td>2.67</td>
</tr>
<tr>
<td>2.59</td>
<td>2.58</td>
<td>2.60</td>
<td>2.60</td>
</tr>
<tr>
<td>2.41</td>
<td>2.42</td>
<td>2.43</td>
<td>2.43</td>
</tr>
<tr>
<td>2.37</td>
<td>2.39</td>
<td>2.40</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Since all the d-spacings match, the sample possessed the
HSAPO-5 structure. Due to the lack of sensitivity of the Guinier-Haegg method, the very weak lines lower than 2.37 Å were not seen.

More information was obtained from the x-ray diffractometer analysis of the HSAPO-5 catalyst sample after the templating molecule had been removed by calcining overnight in air at 500°C. The resulting diffractogram is shown in Figure 10. The sharp peaks indicate that the sample was highly crystalline.

**BET Study**

Characterization of the porous microstructure of HSAPO-5 and other catalysts was accomplished by the BET nitrogen adsorption method. As shown in Figure 11, the linearized BET plot for the zeolitic catalysts deviated from linearity in a way that is typical of microporous solids. The linear region for these solids was at very low $\frac{P}{P^0}$ (less than 0.1), where $P^0$ is the saturation pressure for nitrogen. Since the applicability of the BET method at less than multilayer coverage was in question for these catalysts, all of the surface area calculations were performed on data obtained at $\frac{P}{P^0}$ values less than 0.1 to ensure linearity of the BET equation. Table 4 lists the results of the study.
Linearized BET Plots for Microporous Catalysts

![Graph showing linearized BET plots for different catalysts.]

- H-SAPO-5 0.3707 gms.
- H-AlPO-5 0.1064 gms.
- H-ZSM-5 0.3708 gms.

Figure 11
Table 4  
Catalyst Surface Areas

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin SAPO-5</td>
<td>32</td>
<td>———</td>
</tr>
<tr>
<td>Calcined HSAP-5</td>
<td>237</td>
<td>0.120</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>422</td>
<td>0.241</td>
</tr>
<tr>
<td>HALPO-5</td>
<td>324</td>
<td>0.200</td>
</tr>
<tr>
<td>Houdry M-46</td>
<td>236</td>
<td>———</td>
</tr>
</tbody>
</table>

Note:
1. Intercepts O(10⁻⁶) and slopes O(10⁻¹) for microporous catalysts; thus, BET "C"'s O(10⁵).
2. Total nitrogen adsorption at P/P° of 0.9

Hydrogen-Deuterium Exchange

An upper limit for the active sites was found by exchanging most of the hydrogens on the catalyst surface with deuteriums from benzene molecules in the gas phase. This exchange can occur under other circumstances, i.e. over metals and strong bases. Since the H form of SAPO-5 was used for the catalytic studies and the exchange was performed in the gas phase with only helium present, the only exchange possible was with the hydrogens on the surface.

Initially, the temperature dependency of the exchange reaction was investigated. Usually six pulses of d₆-benzene were injected. The results are seen on Figures 12 through 15. Both Σ, the accumulation of exchanged hydrogens, versus pulse number and their inverses were plotted. The former was plotted to demonstrate the extent of the extrapolation. The latter was plotted to ascertain the applicability of the least squares method. The circles were the actual data.
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data

HSAP0-5
0.5011 grams
320°C

Figure 12(b)

Figure 12(a)
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data

HSAP0-5
0.5023 grams
350°C

Figure 13(b)

Figure 13(a)
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data

HSAPO-5
0.3118 grams
350°C

Figure 14(b)

Figure 14(a)
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data

HSAPo-5
0.1980 grams
380°C

Figure 15(b)

Figure 15(a)
points. The solid lines were the calculated values from the model described in Appendix E. \( \Sigma \) and \( \Sigma_{oo} \) were normalized by dividing by \( n_{bz} \).

Table 5, taken from Figures 12b through 15b, indicated that there was essentially no exchangeable hydrogen concentration temperature dependence. Also, listed in the table are the extrapolated deuterium recovery efficiencies for each run, R. R was the percentage of deuteriums exchanged with the surface that are recoverable by exchange with an infinite number of \( d_0 \)-benzene pulses.

<table>
<thead>
<tr>
<th>T.(°C)</th>
<th>Wt.(g)</th>
<th>( \Sigma_{oo}/n_{bz} )</th>
<th>R(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>0.5011</td>
<td>25.15</td>
<td>92</td>
</tr>
<tr>
<td>350</td>
<td>0.5023</td>
<td>24.29</td>
<td>83</td>
</tr>
<tr>
<td>350</td>
<td>0.3118</td>
<td>25.34</td>
<td>83</td>
</tr>
<tr>
<td>380</td>
<td>0.1980</td>
<td>23.23</td>
<td>85</td>
</tr>
</tbody>
</table>

Notes:
1. Helium flowrate 20 cc/min
2. Normalized with \( n_{bz} \), 1.36*10^{19} benzene molecules/pulse
3. Extrapolated to \( \infty \) pulses of \( d_0 \)-benzene

Using an average value of 24.4 for \( \Sigma_{oo}/n_{bz} \), the surface area for hydrogen atoms was calculated to be 74.9 Å^2 on HSAPO-5.

A comparison study was also conducted over HALPO-5, HZSM-5, and Houdry M-46 silica-alumina. The results are
plotted on Figures 16 through 18. Finally, Table 6 lists the extrapolated values for the exchange study.

Table 6

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T(°C)</th>
<th>( \Sigma /n )</th>
<th>( A^2/H ) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSAPo-5</td>
<td>321</td>
<td>24.9</td>
<td>75.</td>
</tr>
<tr>
<td>HAPO-5</td>
<td>400</td>
<td>11.8</td>
<td>202.3</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>321</td>
<td>60.6</td>
<td>51.</td>
</tr>
<tr>
<td>M-46</td>
<td>350</td>
<td>49.8</td>
<td>35.</td>
</tr>
</tbody>
</table>

Notes:
1 Helium flowrate 20 cc/min
2 Same as note 2 in Table 5

The calculation of \( \Sigma_{\infty} \) was based upon the extrapolation of the scaled variable \( P \)

\[
P = \frac{6 - \phi_j}{6}
\]

where \( \phi_j \) is defined in Appendix E and represents the average number of \( D \) atoms/benzene molecule. For statistical scrambling, the following equation holds for the distribution of deuteriums in the benzene ring

\[
\delta_i = \frac{6!}{i!(6-i)!} P^i (1-P)^{6-i}
\]

where \( P \) is the probability of finding one deuterium substitution in the benzene ring. \( (1-P) \) is the probability of finding one hydrogen in the benzene ring. Since \( \phi_j \) is defined as

\[
\phi_j = \Sigma_{i=0}^{6} (6-i) \delta_i
\]
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data
HALPO-5
0.2379 grams
400°C

Figure 16(b)

Figure 16(a)
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data
HZSM-5
0.2442 grams
321°C

Figure 17(b)

Figure 17(a)
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data

Houdry M-46
0.3131 grams
350°C

Figure 18(b)

Figure 18(a)
Substituting $d_i$ from equation 6 into equation 7,

$$\phi_j = \sum_{i=0}^{6} \frac{6!}{i!(6-i)!} p^i (1-p)^{6-i}$$  \hspace{1cm} (10)$$

or

$$\phi_j = \sum_{i=0}^{5} \frac{5!}{i!(5-i)!} p^i (1-p)^{5-i} (1-p)$$  \hspace{1cm} (11)$$

or

$$\phi_j = 6(1-p) \sum_{i=0}^{5} \frac{5!}{i!(5-i)!} p^i (1-p)^{5-i}$$  \hspace{1cm} (12)$$

or

$$\phi_j = 6(1-p).$$  \hspace{1cm} (13)$$

Thus, the scaled variable $P$ is also the statistical probability. Figures 19 through 22 are checks on a statistical distribution for each pulse over the catalysts studied. The $P$ values listed are the probabilities calculated from the observed values of $\phi$ for each pulse. Only six of the fourteen pulses for HALPO-5 were considered since very little exchange occurred thereafter.
Deuterium Scrambling Patterns

Experimental versus Statistical Distribution

**HSAPO-5**

0.5023 gm 350 °C 20 cc/min

**Pulse 1**

\[ P = 0.14 \]

**Pulse 2**

\[ P = 0.47 \]

**Pulse 3**

\[ P = 0.72 \]

**Pulse 4**

\[ P = 0.87 \]

**Pulse 5**

\[ P = 0.93 \]

**Pulse 6**

\[ P = 0.95 \]

\[ \text{Exp} \quad \text{Stat} \]

Figure 19
Deuterium Scrambling Patterns

Experimental versus Statistical Distribution

HA1PO-5
0.2379gm 400 C 20 cc/m

Pulse 1
P = 0.84

Pulse 2
P = 0.91

Pulse 3
P = 0.95

Pulse 4
P = 0.96

Pulse 5
P = 0.97

Pulse 6
P = 0.98

Figure 20
Deuterium Scrambling Patterns

Experimental versus Statistical Distribution

HZSM-5
0.2442gm 321°C 20 cc/m

Pulse 1
P = 0.00

Pulse 2
P = 0.14

Pulse 3
P = 0.62

Pulse 4
P = 0.90

Pulse 5
P = 0.97

Pulse 6
P = 0.98

Exp  Stat

Figure 21
Deuterium Scrambling Patterns

Experimental versus Statistical Distribution

Houdry M-46
0.3131gm 350°C 20 cc/min

Pulse 1
P = 0.36

Pulse 2
P = 0.40

Pulse 3
P = 0.63

Pulse 4
P = 0.77

Pulse 5
P = 0.85

Pulse 6
P = 0.90

Figure 22
Kinetic Experiments

CSTR Results

Coking, Structure Stability, and Regeneration

Several experiments were run on HSAPO-5 to find the influence of the isomerization reaction on catalyst properties. Specifically, the effects of coking on the surface area, crystallinity, and site density were investigated.

Surface area changes during coking and regeneration are summarized in Table 7. A drastic decrease in surface area and pore volume was seen. However, complete restoration of surface area was possible upon regeneration.

Table 7

<table>
<thead>
<tr>
<th>Rxn. Time(hr)</th>
<th>Area ($m^2/g$)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>240.</td>
<td>0.121</td>
</tr>
<tr>
<td>0.5</td>
<td>220.</td>
<td>0.111</td>
</tr>
<tr>
<td>3.0</td>
<td>80.</td>
<td>0.053</td>
</tr>
<tr>
<td>Rgn. Time(hr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>207.</td>
<td>0.116</td>
</tr>
<tr>
<td>17.0</td>
<td>260.</td>
<td>0.130</td>
</tr>
</tbody>
</table>

Note:

1 Regeneration Conditions: 450°C, 0.33:0.67 O2:He molar ratio, total flow 60 sccm.

Note that complete restoration was not accomplished until overnight calcination was performed.

A hydrogen/deuterium exchange study was performed on the seventeen hour regenerated HSAPO-5. The results are
plotted in Figure 23. As seen in Table 8, complete restoration of the number of exchangeable hydrogen atoms was also accomplished. An exchange study was not carried out on the deactivated catalyst.

Table 8

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(\Sigma /n_{bz})</th>
<th>(A /H) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>25.</td>
<td>75.</td>
</tr>
<tr>
<td>Regen.</td>
<td>23.</td>
<td>86.</td>
</tr>
</tbody>
</table>

Note:
1 Same as Note 2 in Table 5.

Figure 24 is an x-ray diffractogram of a catalyst sample that was coked during an isomerization reaction. As can be seen, no structural degradation occurred since the d-spacings and relative intensities are the same as the fresh catalyst (Figure 10, p. 66).

Coking played an important part in the xylene isomerization rate over HSAPO-5. Figure 25 is a typical plot of xylene conversion versus time on stream. Also plotted are the curves of the same reaction after several regenerations. Consistent with the previous findings of restoration of active site density and surface area, the same time on stream curve was followed.

An objective of the regeneration experiments was to calculate the weight percent of coke on the catalyst. Since the data displayed considerable scatter, a determination of
Determination of Exchangeable Hydrogen
Scaled Variable Extrapolation of Experimental Data
Regenerated HSAP0-5
0.3354 grams
320°C

Figure 23(b)

Figure 23(a)
X-Ray Diffractogram of Coked HSAP0-5

Compare with Figure 10, page 66

Figure 24
Experimental Reproducibility Over HSAP0-5
m-Xylene Isomerization

Feed 13.5 Torr
0.2935 gm
T 26 sec
T 430°C

Run  Symbol
1     □
2     ○
3     △
4     +

m-Xylene Conversion, %

Time on Stream, hr

Figure 25
the rate of coking, grams/hour, was not possible. However, the indirect approach of studying the catalyst activity versus time led to some important observations.

Langner (55) reported a temperature dependent coking mechanism. Viner (56) reported a region of applicability of the time on stream theory. A series of experiments were designed to test these theories.

The following simple time on stream theory was based on a parallel mechanism for coking

\[
\text{ortho} \rightarrow \text{meta} \rightarrow \text{para} \\
\uparrow \quad \uparrow \quad \uparrow \\
\text{C} \quad \text{O} \quad \text{K} \quad \text{E}
\]

The coking variable, \(a\), was defined as the ratio of the observed rate to the initial rate, i.e.

\[
a = \frac{r_m}{r_0} \quad 14).
\]

Thus, the observed reaction rate for a first order reaction equals

\[
r_m = k \cdot a \cdot P \quad 15).
\]

It is also assumed that the coking rate is linearly dependent on the xylene concentration, viz.

\[
\frac{da}{dt} = k_d (P_m + P_P + P_O) a \quad 16)
\]

where \(k_d\) was the activity decay constant. Since there is no
mole change during the isomerization reaction, \((P_m + P_p + P_o)\) is constant. Thus,

\[
\frac{-\text{d}a}{\text{d}t} = k'_a a
\]

17)

or

\[
a = e^{-k'_a t}
\]

18)

since at time zero, \(a\) is unity. Thus, a plot of \(\ln(a)\) versus time on stream should be linear with slope \(-k'_a\).

Figure 26 shows the effect of temperature on coking. The time on stream theory seemed to apply over reaction times of less than ten hours.

By fitting the curve to equation 18, values for \(k'_a\) were calculated; they are listed in Table 9. Evidence for different coking mechanisms was seen for times greater than ten hours. An Arrhenius plot of the preceding constants is shown in Figure 27. The resulting activation energy calculated from the slope is \(-24.5 \text{ kcal/mole}\). This implies that at higher temperatures for low time on stream values, the rate of activity loss decreases.

Table 9

| m-Xylene Isomerization Activity Decay Constants (hr\(^{-1}\)) Over HSAPO-5 |
|-----------------------------|-----------------|
| **Temp. (°C)**            | **\(k'_a\)**   |
| 388                        | 0.120           |
| 408                        | 0.073           |
| 448                        | 0.024           |
| 483                        | 0.012           |
Time on Stream Decay Functions
m-Xylene Isomerization Over HSAP0-5

Feed 13.5 Torr
0.2935 gm
\( \tau \) 24.9 sec

Figure 26
m-Xylene Isomerization Over HSAPO-5

Arrhenius Plot of Activity Decay Constants

Figure 27
Initial Conversion Data

The analysis in Appendix D indicates that diffusion did not influence the reaction rate. However, coking played an important role. Usually kinetic analyses are made on a catalyst after it has reached a constant "reference level" of activity. As can be seen from Figure 25, such a region of constant activity was never achieved for HSAPO-5. Thus, only experiments involving initial rate data were used in the kinetic studies. In order to obtain enough points for a smooth curve, experiments were run for four hours. Using the time on stream decay functionality, the logarithm of the partial pressures were plotted versus the reaction time. The initial conversion was then found by extrapolation. An example of this is seen in Figure 28. Note that the low partial pressures of transalkylation products, i.e. toluene, hemellitene, mesitylene, and pseudocumene, are multiplied by a factor of ten. This method led to conversion values free from the influence of coking. Thus, results from different temperatures and inlet partial pressures could be compared directly.

Some of the data from the initial conversion experiments are tabulated in Tables 21 and 22 in Appendix G. Very little transalkylation (to toluene and trimethylbenzenes) was seen. Generally, less than 6% of the inlet feed was converted to the disproportionation products over the
Initial Data Extrapolation Example

Meta-xylene Isomerization

Trxn = 381°C

Figure 28
temperature range of the initial data study, i.e. 320-340°C. Only trace amounts of benzene were seen.

Xylene Isomerization Model

The xylene isomerization reaction pathway was considered. In order to determine whether the pathway is a series, triangular, or common intermediate process, several experiments were run on o-xylene. If direct ortho to para conversions were allowed, then a triangular or common intermediate model would be applicable. If they were not allowed, then the series mechanism would hold. Figure 29 is a plot of the xylene product selectivity versus the conversion of the feed o-xylene, taken from data in Table 22 in Appendix G. Clearly at zero+ conversions, no p-xylene was formed. Thus, xylene isomerization over HSAPO-5 appears to be a series process.

Next, the order of the reaction was considered. Most of the literature data indicate that the xylene isomerization reactions are first order in the distance from equilibrium. For a first order reaction, the fractional conversion does not depend on feed partial pressure. Table 10 lists the conversions from experiments performed by varying the feed partial pressures of meta-xylene. Within experimental error, the conversions did not vary with inlet feed concentration. This is consistent with first order behavior.
Verification of Series Mechanism
Isomerization of o-Xylene Over HSAP0-5

<table>
<thead>
<tr>
<th>Point</th>
<th>Temp. (°C)</th>
<th>Weight (gms)</th>
<th>Feed (Torr)</th>
<th>Feed (torr g s/mole)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>361</td>
<td>0.2058</td>
<td>12.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>344</td>
<td>0.3000</td>
<td>19.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>363</td>
<td>0.3000</td>
<td>19.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>420</td>
<td>0.3000</td>
<td>19.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>437</td>
<td>0.3000</td>
<td>19.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 29
Table 10

m-Xylene
Initial Conversion Dependence
on Feed Partial Pressure
Over HSAPO-5

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>13.5</th>
<th>18.9</th>
<th>26.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>359</td>
<td>19.3</td>
<td>17.8</td>
<td>17.6</td>
</tr>
<tr>
<td>380</td>
<td>----</td>
<td>26.0</td>
<td>----</td>
</tr>
<tr>
<td>398</td>
<td>33.1</td>
<td>31.8</td>
<td>32.0</td>
</tr>
<tr>
<td>420</td>
<td>39.4</td>
<td>38.9</td>
<td>38.5</td>
</tr>
<tr>
<td>438</td>
<td>45.5</td>
<td>45.8</td>
<td>44.7</td>
</tr>
</tbody>
</table>

Flow

1.9

2.7

3.8

Flow

Notes:

1. 0.3034 gm catalyst, \( \eta = 7660 \text{ torr} \cdot \text{g} \cdot \text{s} \) mole

2. In \( \text{mmoles} \) hr

Using meta as feed, the isomerization reaction may be written as

\[
P \xrightarrow[1]{} \text{m} \xrightarrow[2]{} \text{m}
\]

For a steady state CSTR reactor and pure meta feed, \( P_m^o \) (partial pressure in helium diluent, torr), the reaction rates, \( r_i \)'s \( \left( \frac{\text{mole}}{\text{g} \cdot \text{s}} \right) \), for the three compounds are

\[
r_m = \frac{P_m^o - P_m}{\eta} = (k_2 + k_3)P_m - k_1P_0 - k_4P_0
\]
\[ r_p = \frac{P_p}{\eta} = k_2 P_m - k_1 P_p \]  

\[ r_o = \frac{P_o}{\eta} = k_3 P_m - k_4 P_o \]

The reaction rates are defined as in Appendix B. Here \( \eta \) is the space time (\( \tau \) from Appendix B) times \( W \), the weight of the catalyst, divided by \( V_r \), the volume of the reactor. Hence, the rate constants, \( k_i \)s, depend on the catalyst weight. When these equations are solved algebraically, the following relationships can be derived

\[ \frac{P_m}{P_m^0} = \frac{1}{1 + \frac{k_3 \eta}{1+k_4 \eta} + \frac{k_2 \eta}{1+k_1 \eta}} \]  

\[ \frac{P_p}{P_m^0} = \frac{k_2 \eta}{1+k_1 \eta} \]

\[ \frac{P_o}{P_m^0} = \frac{k_3 \eta}{1+k_4 \eta} \]

\[ \frac{1}{1 + \frac{k_3 \eta}{1+k_4 \eta} + \frac{k_2 \eta}{1+k_1 \eta}} \]
Using ortho as feed, the reaction may be written as

$$
\begin{array}{c}
1 & 3 \\
\rightarrow & \rightarrow \\
p & m & o \\
2 & 4 \\
\end{array}
$$

Writing similar mass balance and mass action kinetic equations for each compound and solving the set algebraically, the following equations for the concentration result.

$$
\frac{P_O}{P^o} = \frac{\frac{1}{\eta} + \frac{k_1 k_3}{1 + k_1 + k_2 + k_3}}{1 + k_4 - \frac{k_3 (k_4 - k_1)}{\eta}}
$$

$$
\frac{P_m}{P^o} = \frac{k_4 \eta}{1 + k_4 \eta} \\
\frac{P_d}{P^o} = \frac{(\frac{k_2 \eta}{1 + k_1 \eta})(\frac{k_4 \eta}{1 + k_4 \eta})}{1 + \frac{k_2 \eta}{1 + k_1 \eta} + \frac{k_3 \eta}{1 + k_4 \eta}}
$$
Had the reactions occurred via a series, rather than a triangular, network with first order mass action kinetics, the data for the xylenes should fit these equations.

Only xylenes were considered in the non-linear regression curve fitting. Also, since a constant "reference level" activity was never reached, the data used in the regression analysis were the "initial rate" values. One reaction temperature was considered for o-xylene to check the consistency of the equations developed. Figures 30 through 34 result from the curve fitting. As can be seen, the first order series model fits the data very well.

Table 11 lists the reaction constants calculated for the meta-xylene isomerization reactions. Only the forward reaction rate constants are listed since the reverse constants are related through the equilibrium constants.

Table 11
Isomerization Reaction Rate Constants
Over HSAPO-5

\[
\text{mole} \quad \left( \frac{\text{mole}}{\text{g} \cdot \text{s} \cdot \text{torr}} \right)
\]

<table>
<thead>
<tr>
<th>m-Xylene Feed</th>
<th>( k_2 \times 10^6 )</th>
<th>( k_3 \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T , (^\circ \text{C}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>324</td>
<td>3.7</td>
<td>8.3</td>
</tr>
<tr>
<td>347</td>
<td>7.14</td>
<td>14.5</td>
</tr>
<tr>
<td>359</td>
<td>11.1</td>
<td>23.5</td>
</tr>
<tr>
<td>382</td>
<td>22.7</td>
<td>39.7</td>
</tr>
</tbody>
</table>
Model versus Experimental Results
meta-Xylene Isomerization Over HSAP0-5

Trxn = 324°C

<table>
<thead>
<tr>
<th>Point</th>
<th>Feed (torr)</th>
<th>Weight (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>0.2058</td>
</tr>
<tr>
<td>2</td>
<td>12.6</td>
<td>0.3000</td>
</tr>
<tr>
<td>3</td>
<td>18.9</td>
<td>0.3034</td>
</tr>
<tr>
<td>4</td>
<td>15.1</td>
<td>0.6004</td>
</tr>
</tbody>
</table>

Figure 30
Model versus Experimental Results
meta-Xylene Isomerization Over HSAP0-5

Trxn = 347°C

<table>
<thead>
<tr>
<th>Point</th>
<th>Feed (torr)</th>
<th>Weight (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>0.2058</td>
</tr>
<tr>
<td>2</td>
<td>12.6</td>
<td>0.3000</td>
</tr>
<tr>
<td>3</td>
<td>18.9</td>
<td>0.3000</td>
</tr>
<tr>
<td>4</td>
<td>18.9</td>
<td>0.4000</td>
</tr>
<tr>
<td>5</td>
<td>15.1</td>
<td>0.6004</td>
</tr>
</tbody>
</table>

Figure 31
Model versus Experimental Results
meta-Xylene Isomerization Over HSAP0-5

Trxn = 359°C

<table>
<thead>
<tr>
<th>Point Feed Weight</th>
<th>(torr)</th>
<th>(gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>0.2058</td>
</tr>
<tr>
<td>2</td>
<td>12.6</td>
<td>0.3000</td>
</tr>
<tr>
<td>3</td>
<td>18.9</td>
<td>0.3034</td>
</tr>
<tr>
<td>4</td>
<td>15.1</td>
<td>0.6004</td>
</tr>
</tbody>
</table>

Figure 32
Model versus Experimental Results
Meta-xylene Isomerization Over HSAP0-5

\( \text{Trxn} = 382^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Point</th>
<th>Feed Weight (torr)</th>
<th>(gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>0.2058</td>
</tr>
<tr>
<td>2</td>
<td>12.6</td>
<td>0.3000</td>
</tr>
<tr>
<td>3</td>
<td>18.9</td>
<td>0.3034</td>
</tr>
<tr>
<td>4</td>
<td>18.9</td>
<td>0.4030</td>
</tr>
<tr>
<td>5</td>
<td>15.1</td>
<td>0.6004</td>
</tr>
</tbody>
</table>

**Figure 33**
Model versus Experimental Results
ortho-Xylene Isomerization Over HSAP0-5

Trxn = 362°C

<table>
<thead>
<tr>
<th>Point</th>
<th>Feed Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(torr)</td>
</tr>
<tr>
<td>1</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>24.6</td>
</tr>
<tr>
<td>3</td>
<td>19.1</td>
</tr>
<tr>
<td>4</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Figure 34
An Arrhenius plot of the rate constants is shown in Figure 35. The resulting activation energies and their errors for the forward reactions are

\[
m \rightarrow p \quad 24.4 \pm 0.6 \text{ kcal/mole} \quad \text{and} \quad m \rightarrow o \quad 21.4 \pm 0.7 \text{ kcal/mole}.
\]

The errors were calculated from the differences between the least squares line and the actual data points.

In Figure 36, the same data as shown in Figures 30 through 34 are replotted collectively at constant modified space velocity. The reaction temperature is plotted along the abscissa. This plot was constructed to determine the change in selectivity with temperature. The solid lines were calculated by using equation 22 with the resulting constants from Table 11. The dotted lines represent 10 and 20% conversion. The intersection of the dotted lines and the solid curves gives the reaction temperature and the \( \eta \)'s which will result in the desired conversion. The intersections are plotted in Figure 37. Here the p-selectivity is defined as the ratio of produced p-xylene to the sum of produced p- and o-xylene. For HSAP0-5, it is apparent that the p-selectivity observed is less than the thermodynamic equilibrium selectivity.
Xylene Isomerization Over HSAP0-5
Arrhenius Plot of First Order Constants

Figure 35
m-Xylene Isomerization Over HSAP0-5

Effect of Reaction Temperature and $\eta$
Experimental versus Model

Curve $\eta$ (torr g s/mole)
- □ 3400
- ○ 5000
- △ 7500
- + 10000
- × 12000

Figure 36
m-Xylene Isomerization
Constant Conversion Selectivities
Over HSAP0-5

Figure 37
Disproportionation Model

At the reaction temperatures used in this study, less than 6% of the xylenes was converted to disproportionation products. At these low conversions, due to the limited accuracy of the data, it was not possible to develop an exact model of the individual reactions.

To test the reversibility of disproportionation over HASPO-5, several tests were conducted. Table 12 lists the results of the pulse injections over the catalyst.

Table 12
Disproportionation\(^1\) Reversibility Over HSAPO-5

\[
\text{20} \quad \frac{\text{cc}}{\text{min}} \text{He, 0.2163 gm}
\]

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Feed</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bz</td>
</tr>
<tr>
<td>350</td>
<td>Mix(_2) (^2)</td>
<td>----</td>
</tr>
<tr>
<td>375</td>
<td>Mix(_2) (^2)</td>
<td>----</td>
</tr>
<tr>
<td>400</td>
<td>Mix(_2) (^2)</td>
<td>----</td>
</tr>
<tr>
<td>425</td>
<td>Mix(_2) (^2)</td>
<td>----</td>
</tr>
<tr>
<td>450</td>
<td>Mix</td>
<td>0.01</td>
</tr>
<tr>
<td>450</td>
<td>TMB(^3)</td>
<td>----</td>
</tr>
<tr>
<td>450</td>
<td>Tol</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Notes:
1. Thermally neutral system, i.e. Tol:Xylene:3MB equilibrium is 0.27:0.46:0.27
2. 2 µliter 50:50 (Molar) pulse of Toluene:1,2,4-Trimethylbenzene
3. 2 µliter pulse of 1,2,4-Trimethylbenzene
4. Tol:meta:ortho ratio was 0.02:0.30:0.68
5. Trimethylbenzenes
6. Tetramethylbenzenes
The overall disproportionation reaction followed can be written as

\[ 5 \text{A} \rightleftharpoons 2 \text{B} + \text{C} \]

where A, B, and C represent the combined xylenes, toluene, and total trimethylbenzenes, respectively.

For a CSTR, the following mass action reaction rate equation can be written for the xylenes

\[ r_a = \frac{p_a^0 - p_a}{\eta} = k_5 p_a^{2} k_5 p_b p_c \]

The same terminology as used in equations 19-21 was followed. Defining the overall conversion of xylenes to the disproportionation product as

\[ X = \frac{p_a^0 - p_a}{p_a^0} \]

substituting into equation 29, and solving algebraically for X yields the result

\[ X = \frac{2 + \frac{1}{k_1 p_a^0 \eta} - \sqrt{4 + \frac{1}{k_1 p_a^0 \eta} + \left(\frac{1}{k_1 p_a^0 \eta}\right)^2}}{2 \left(1 - \frac{1}{4k_{eq}}\right)} \]

where \( k_{eq} = \frac{k_5}{k_5'} \).

Using the data in Appendix G and the minimization routines applied in the xylene isomerization study, values for \( k_1 \) were calculated. Table 13 lists the results. An Arrhenius plot of the reaction constants is shown in Figure 38. The resulting activation energy is 8.5 kcal/mole.
Xylene Disproportionation Over HSAP0-5

Arrhenius Plot of Second Order Constants

Figure 38
Table 13

Disproportionation Reaction Rate Constants
Over HSAGO-5

\[
\frac{\text{mole}}{\text{g} \cdot \text{s} \cdot \text{torr}^2}
\]

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>(k_1)</th>
<th>(K_{eq}^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>2.65*10^{-7}</td>
<td>0.323</td>
</tr>
<tr>
<td>340</td>
<td>3.96*10^{-7}</td>
<td>0.323</td>
</tr>
<tr>
<td>380</td>
<td>5.33*10^{-7}</td>
<td>0.323</td>
</tr>
</tbody>
</table>

Note:

\(K_{eq}\) does not change significantly in this temperature range.

Microcatalytic Reactor Results

\(^{13}\)C Label Experiments

A simple and quite straightforward method of determining the nature of the isomerization mechanism is to isomerize a mixture of non-labeled o-xylene and o-xylene labeled in both methyl groups with \(^{13}\)C. The feed was a 50:50 mixture of unlabeled ortho-xylene and \(^{13}\)C labeled ortho-xylene with an isotopic purity of 99.5%.

If the mechanism were strictly intramolecular, then mass spectra of the isomerization products would show a one to one m/e ratio for the 106 and 108 species. On the other hand, if the mechanism were purely intermolecular, then the products would show a 1:2:1 ratio of the m/e peaks 106, 107, and 108, respectively. The m/e of 107 is twice as large as
the others since that isomer could be produced from both labeled and non-labeled o-xylene feed.

The fraction of inter behavior was defined as the following product mole ratio

\[
\frac{\text{mole fraction 107}}{\text{mole fraction (106+108)}}
\]

For a purely intramolecular mechanism, the ratio is zero. A purely intermolecular mechanism would give a ratio of unity.

Experiments were conducted on a series of four catalysts to see if structure or acid strength influenced the mechanism. Figure 39a shows the results. The accuracy of the ratio at low conversions was adversely affected by the small sample size which made it difficult to trap and analyze the products quantitatively. Nevertheless, it is clear that over all of the catalysts the mechanism is intramolecular. The sharp increase in inter behavior at high conversions over HSAPO-5 is characteristic of the reversible and obviously intermolecular disproportionation reactions. This can be seen in Figure 39b from the sharp rise the toluene mole fraction in the pulse experiments.
$^{13}$C Labeling Experiments

![Graph showing $^{13}$C labeling experiments](image)

**Figure 39(b)**

![Graph showing o-Xylene conversion and fraction inter behavior](image)

- **HA1PO-5**
- **HSAPO-5**
- **HZSM-5**
- **Houdry M-46**
- **Silica-Alumina**

**Figure 39(a)**
Deuterium Label Experiments

Deuterium scrambling experiments were conducted over the catalysts to determine the exchange of H atoms among molecules and with the catalyst. The feed mixture involved a combination of deuterium labeled and non-labeled aromatic compounds.

A series of pulses of a mixture containing d₀ and d₁₀-o-xylene (50:50, molar ratio) were passed over the catalyst. The atoms exchanged per molecule, φ, was used to characterize the extent of scrambling. It is defined as follows

\[
\phi = \sum_{i=0}^{5} i \times d_i + \sum_{i=6}^{10} (10-i) \times d_i
\]

In a statistical distribution of the 10 H and D positions on a xylene molecule, φ would be 3.82; one involving the aryl hydrogens only would result in a φ of 2. Table 14 lists the results obtained over the series of catalysts. Evident is the lack of a statistical distribution of the ten positions over a wide range of temperatures and carrier flowrates. Also, no channeling through the reactor bed occurred since there was a very small change in φ with large changes in carrier flowrates. Table 15 lists the deuterated isomer mole fractions over HSAPo-5, HAlPO-5, and the statistical distribution values.

The question of aryl versus methyl hydrogen exchange was pursued further. Cumene has five aryl hydrogens and
Table 14
Scrambling of o-Xylene Mixture
Over Various Catalysts and Conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature °C</th>
<th>Carrier Flow (cc/min)</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSAPO-5</td>
<td>400</td>
<td>3000</td>
<td>2.1</td>
</tr>
<tr>
<td>0.2450 gm</td>
<td>300</td>
<td>3000</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3000</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>3000</td>
<td>2.0</td>
</tr>
<tr>
<td>HALPO-5</td>
<td>150</td>
<td>339</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2260 gm</td>
<td>300</td>
<td>38</td>
<td>2.0</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>150</td>
<td>339</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2500 gm</td>
<td>150</td>
<td>38</td>
<td>2.0</td>
</tr>
<tr>
<td>M-46</td>
<td>150</td>
<td>3000</td>
<td>1.8</td>
</tr>
<tr>
<td>0.2515 gm</td>
<td>150</td>
<td>1550</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1050</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>113</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>20</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 15
Scrambling of o-Xylene Mixture
Comparison of Experimental with Statistical Distribution
at T 150°C

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Statistical Distribution</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All</td>
<td>Aryl</td>
</tr>
<tr>
<td>10</td>
<td>0.001</td>
<td>0.032</td>
</tr>
<tr>
<td>9</td>
<td>0.010</td>
<td>0.124</td>
</tr>
<tr>
<td>8</td>
<td>0.044</td>
<td>0.188</td>
</tr>
<tr>
<td>7</td>
<td>0.117</td>
<td>0.124</td>
</tr>
<tr>
<td>6</td>
<td>0.205</td>
<td>0.032</td>
</tr>
<tr>
<td>5</td>
<td>0.246</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.205</td>
<td>0.032</td>
</tr>
<tr>
<td>3</td>
<td>0.117</td>
<td>0.124</td>
</tr>
<tr>
<td>2</td>
<td>0.044</td>
<td>0.188</td>
</tr>
<tr>
<td>1</td>
<td>0.010</td>
<td>0.124</td>
</tr>
<tr>
<td>0</td>
<td>0.032</td>
<td>0.032</td>
</tr>
</tbody>
</table>

φ 3.8  2.0  2.0  2.0

Notes:
\textsuperscript{1} T=150°C, 300 cc/min He, 0.2260 gm
\textsuperscript{2} T=150°C, 3000 cc/min He, 0.2450 gm
seven non-aryl hydrogens. An experiment was run under conditions where no dealkylation reaction occurred. A mixture of cumene and \( d_6 \)-benzene (1:10, molar H:D ratio) was passed over ZSM-5 covered with deuteriums. Both compounds were trapped and analyzed. Table 16 lists the results.

Table 16
Cumene/\( d_6 \)-Benzene Exchange\(^1\) Over HZSM-5

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Mole Fractions</th>
<th>Statistical Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzene</td>
<td>Cumene</td>
</tr>
<tr>
<td>( i )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.786</td>
<td>0.005</td>
</tr>
<tr>
<td>5</td>
<td>0.191</td>
<td>0.724</td>
</tr>
<tr>
<td>4</td>
<td>0.023</td>
<td>0.233</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.038</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( \phi \) | 0.24          | 4.7                      | 6                 |

Note:
1. \( T=150^\circ \)C, 180 cc/min He, 0.2018 gm
2. All twelve hydrogens on cumene

Very little exchange was expected and seen for \( d_6 \)-benzene since it was present in large excess. However, the prominent fact from the table is that there is essentially no exchange above five positions. Again, this confirms the suspicion that only aryl hydrogens exchange in the alkylaromatics.
Having analyzed the exchange results under conditions of no reaction, we ran some xylene isomerization experiments to explore the effect of reaction on the value of $\phi$ for the products and reactants. Figure 40 illustrates the results over HSAPO-5 at 400°C. There is a difference of 0.4 between the product and reactant $\phi$ over a large range of conversions. Figure 41 indicates that the difference does not change much with temperature over HSAPO-5. As can be seen from Figure 42, over HZSM-5 and amorphous Houdry M-46, the difference in $\phi$ between the products and reactants is smaller (approx. 0.2) than observed on the HSAPO-5 catalyst (approx. 0.4).

Comparison Studies

In order to compare the reactivities of the xylene molecules, a series of pulse experiments were run on the three isomers over HSAPO-5. The results are shown in Table 17. Some important observations can be seen. Ortho-xylene has the highest isomerization to disproportionation ratio. However, p-xylene is more reactive than the other xylenes, the order of reactivity being $p > m > o$.

Table 18 lists the results of a series of experiments run on the catalysts to study their relative catalytic activities. As expected from the exchangeable hydrogen studies, HAlPO-5 has the lowest activity of the series of catalysts and HZSM-5 the highest. At the higher temperatures, the total conversion of the xylene reactants over
Deuterium Scrambling Over HSAP0-5
o-Xylene Isomerization
400°C 0.245 gms.
Equilibrium Conversion 89%
Deuterium Scrambling Over HSAP0-5
o-xylene Isomerization
0.3579 gm

![Graph showing deuterium scrambling over HSAP0-5 o-xylene isomerization with different temperatures.]

Figure 41
Deuterium Scrambling Over HZSM-5 and M-46
o-Xylene Isomerization
400°C
Equilibrium Conversion 89%

![Graph showing deuterium scrambling over HZSM-5 and M-46]

Figure 42
HSAP0-5 equals the total conversion over HZSM-5. However, this is at the expense of the transalkylation reaction as seen by the larger I/D ratio for HSAP0-5.

Table 17
Comparative Reactant Pulse Study
Over HSAP0-5

<table>
<thead>
<tr>
<th>Xylene Feed</th>
<th>Mole Fraction</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>p  m  o</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>0.05 0.32 0.63</td>
<td>38</td>
<td>18</td>
</tr>
<tr>
<td>375</td>
<td>0.10 0.46 0.44</td>
<td>58</td>
<td>13</td>
</tr>
<tr>
<td>400</td>
<td>0.16 0.52 0.32</td>
<td>71</td>
<td>8</td>
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</table>

<table>
<thead>
<tr>
<th>Xylene Feed</th>
<th>Mole Fraction</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>p  m  o</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>0.63 0.31 0.06</td>
<td>46</td>
<td>2</td>
</tr>
<tr>
<td>375</td>
<td>0.47 0.43 0.20</td>
<td>62</td>
<td>2</td>
</tr>
<tr>
<td>400</td>
<td>0.32 0.51 0.17</td>
<td>76</td>
<td>2</td>
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</table>

<table>
<thead>
<tr>
<th>Xylene Feed</th>
<th>Mole Fraction</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>p  m  o</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>0.10 0.76 0.15</td>
<td>29</td>
<td>4</td>
</tr>
<tr>
<td>375</td>
<td>0.16 0.64 0.20</td>
<td>41</td>
<td>4</td>
</tr>
<tr>
<td>400</td>
<td>0.21 0.58 0.21</td>
<td>50</td>
<td>3</td>
</tr>
</tbody>
</table>

Notes:
1 Pulse size was 2μleters; Helium flow was 20 cc/min over 0.2888 gm catalyst.
2 Maximum theoretical conversions varied little with T and was 89%
3 I/D is the ratio of isomerization and disproportionation products
Table 18
Comparative Catalyst Pulse Study

Reaction Temperature 350°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>p</th>
<th>m</th>
<th>o</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALPO-5</td>
<td>0.0</td>
<td>0.02</td>
<td>0.98</td>
<td>2</td>
<td>∞</td>
</tr>
<tr>
<td>M-46</td>
<td>0.02</td>
<td>0.18</td>
<td>0.80</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>HSAPO-5</td>
<td>0.03</td>
<td>0.34</td>
<td>0.63</td>
<td>41</td>
<td>7</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>0.21</td>
<td>0.52</td>
<td>0.27</td>
<td>734</td>
<td>35</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.24</td>
<td>0.53</td>
<td>0.23</td>
<td>89</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Reaction Temperature 400°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>p</th>
<th>m</th>
<th>o</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALPO-5</td>
<td>0.0</td>
<td>0.04</td>
<td>0.96</td>
<td>4</td>
<td>∞</td>
</tr>
<tr>
<td>M-46</td>
<td>0.07</td>
<td>0.37</td>
<td>0.56</td>
<td>46</td>
<td>9.4</td>
</tr>
<tr>
<td>HSAPO-5</td>
<td>0.17</td>
<td>0.52</td>
<td>0.31</td>
<td>70</td>
<td>11</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>0.24</td>
<td>0.51</td>
<td>0.25</td>
<td>75</td>
<td>--</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.24</td>
<td>0.52</td>
<td>0.24</td>
<td>89</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Reaction Temperature 450°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>p</th>
<th>m</th>
<th>o</th>
<th>Overall Conversion</th>
<th>I/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALPO-5</td>
<td>0.0</td>
<td>0.06</td>
<td>0.94</td>
<td>6</td>
<td>∞</td>
</tr>
<tr>
<td>M-46</td>
<td>0.15</td>
<td>0.47</td>
<td>0.38</td>
<td>64</td>
<td>9</td>
</tr>
<tr>
<td>HSAPO-5</td>
<td>0.22</td>
<td>0.54</td>
<td>0.24</td>
<td>79</td>
<td>4</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>0.22</td>
<td>0.54</td>
<td>0.24</td>
<td>77</td>
<td>21</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.23</td>
<td>0.52</td>
<td>0.25</td>
<td>89</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Note:
1 Pulses were 2 μliters of o-xylene; Helium flow was 20 cc/min.
2 Catalyst weight was 0.3 grams.
3 I/D is the ratio of isomerization and disproportionation products.
4 Overall conversion including both isomerization and disproportionation.
IV. Discussion

Catalyst Characterization

One of the major objectives of this study was to synthesize SAPO-5. It is clear from the d-spacings, Table 3, and the x-ray diffractogram, Figure 10, that highly crystalline SAPO-5 was produced. The difference between the Si:Al:P molar ratio in the feed, 0.4:0.3:0.3, and the final catalyst, 0.1:0.56:0.34, was probably due to the crystallization kinetics. Although important, they were not considered relevant to this study in which only one sample of SAPO-5 was required.

Several observations are possible from the BET and H/D exchange studies. First, exchange is rapid and a statistical distribution among the aryl hydrogens was reached for each pulse. In fact, scrambling occurred rapidly at temperatures much lower than those required for isomerization (Table 14). This is consistent with carbenium ion mechanisms where the rate limiting step is not the cleavage of a C-H bond. Secondly, the surface area (Table 7), pore volume (Table 7), and mean H-atom area density (Table 8) can be recovered by regeneration. This is consistent with the fact that no major structural changes occurred during reaction, as indicated by the lack of major differences between the x-ray diffractograms in Figures 10 and 24. Others (21) have also reported the extreme temperature stability of HSAPO-5.
Thirdly, the H-atom densities of this series of catalysts were within an order of magnitude of each other (Table 6). As reported by Hall et al. (101), H-atom concentration is a function of pretreatment temperature. Since only one temperature was used to pretreat the four catalysts, the results should be comparable.

In all of the exchangeable hydrogen pulse experiments, the scaled variable, rather than the least squares, extrapolation method modeled the experimental data more accurately. The $\Sigma$'s calculated by using the scaled variable technique for HALPO-5, HSAPO-5, HZSM-5, and Houdry M-46 are, respectively

$$0.5, 1.3, 2.0, \text{ and } 2.9 \times 10^{14} \frac{\text{H-atom}}{\text{cm}^2}$$

or alternately,

$$1.6, 3.3, 8.2, \text{ and } 6.8 \times 10^{20} \frac{\text{H-atom}}{\text{gram}}.$$

These compare favorably with the values reported in Table 2 on a per gram basis. The large recoveries (greater than 83%) of the exchangeable hydrogens indicate that all H atoms on the surface are readily accessible.

As mentioned by Lok (89), there can be a range of acid strengths over a particular catalyst surface. A hydrogen that possesses the acidity to isomerize xylene will certainly be counted by the exchange method. However, other weaker hydrogens will also be counted. Thus, the exchange-
able hydrogen concentration is an upper bound for the true concentration of the isomerization sites.

Since the highest temperature the catalyst was exposed to was 450°C (during pretreatment), only low levels of Lewis sites were formed. Thus, the active sites are presumed to be Brønsted sites of the type shown on page 28. This is in agreement with Haag (65) for the active site on HZSM-5 and is the same conclusion reached by Ward and Hansford (102) for o-xylene isomerization over amorphous silica-alumina using IR analysis of pyridine adsorption.

The catalyst ranking, on an \( \frac{\text{H-atom}}{\text{cm}^2} \) decreasing basis, is

Houdry M-46 > HZSM-5 > HSAPO-5 > HALPO-5.

The placement of M-46 at the beginning of the list could be due to the increased H-atom density resulting from exchange with terminal silica and alumina groups in the amorphous structure. These groups, however, are not catalytically active. They are not present in crystalline samples.

The trends in deactivation, as indicated by Figures 25 and 26, follow Azuaje's (98) and Gendy and Pratt's (37) pattern of a decreasing deactivation parameter with increasing temperature. The negative activation energy of -24.5 \( \frac{\text{kcal}}{\text{mole}} \) calculated from the slope of the plot in Figure 27 is quite different from the value of -1.34 \( \frac{\text{kcal}}{\text{mole}} \) from (98). Since the deactivation constants obtained by Gendy and Pratt showed
considerable scatter, an activation energy could not be calculated from their data.

A possible explanation for the lower value found by Azuaje is that his deactivation study was performed by injecting reactant pulses over the catalyst, whereas the deactivations for this study were performed by a steady-state reactant flow over the catalyst. The rate and extent of deactivation is expected to be lower in the pulse study.

**Reaction Mechanisms**

**Xylene Isomerization**

An accepted (52,103,104,105) acid catalyzed xylene isomerization mechanism is illustrated in Figure 43. This mechanism involves the protonation of the aromatic ring. The exact location of the addition of the hydrogen is difficult to determine since the resonance of the aromatic structure will delocalize the resulting positive charge. A probable location is used for illustrative purposes. Once the stable cation is formed, a 1,2-methyl shift can occur. Finally, a hydrogen is returned to the catalyst surface and the isomerized molecule is released into the gas phase. Note that this mechanism requires removal of a hydrogen different from the one that protonated the ring.

The kinetic and labeling results of this study are consistent with the proposed mechanism. An intramolecular, acid-catalyzed, 1,2-methyl shift mechanism for xylene isomerization was clearly indicated by the $^{13}$C label experi-
Intramolecular Isomerization Mechanism
(ref. 52, 103, 104, 105)

Figure 43
ments (Figure 39) and the extrapolated o-xylene isomerization experiments (Figure 29).

The activation energies for the m→p and m→o conversions (24.4 and 21.4 kcal/mole, respectively) compare favorably with Hanson and Engel's (22) values of 25.1 and 25.4 kcal/mole over amorphous silica-alumina. Corma and Cortes (53) reported activation energies of 22.8 and 22.3 kcal/mole for the same processes over Ni loaded amorphous silica-alumina. However, the values over HSAPO-5 are lower than the results reported by Miklosy (32) over the small pore Mordenite (36 and 34 kcal/mole). The 6.7Å pores place larger steric limitations on the isomerization reactions, presumably making them harder to occur and raising their activation energies.

A lack of shape selectivity in xylene isomerization over HSAPO-5 can be deduced from Figure 37. Although there is a slight rise in the constant conversion p-selectivity with reaction temperature and activity, it is consistently lower than the thermodynamic value. This is a possible consequence of the large pore size of HSAPO-5, 8Å. The rise in the p-selectivity with temperature is a result of the higher m→p activation energy since that process would be favored at higher temperatures.

To compare the xylene isomerization activities of the catalysts, the data in Table 18 were used to calculate the temperature at which 10% conversion would occur by using the simple method mentioned by Azuaje (98). The analysis
assumes a first order reversible reaction model. This model can be used by combining all of the products of the reaction and observing only the feed xylene.

The final equation is the following

\[
T = \frac{-E_a}{R} \ln \left( \frac{-X}{k_o \ln \left( \frac{X}{X_e} \right)} \right)
\]

where \( T \) is in K, \( E_a \) is the activation energy for the process, \( R \) is the gas constant, \( k_o \) is the forward reaction constant, \( X_e \) is the equilibrium conversion, and \( X \) is the conversion. The activation energies calculated for this model are meaningless since the actual reaction scheme is not as simple as the model assumes. However, trends can be charted by the simple model. Remarkably, the data fit Arrhenius plots of the \( k_o \) data rather well.

As can be seen from Figure 44, there is a big difference in the catalytic activities. This is evident by the fact that there is a 400° temperature range from HALPO-5 to HZSM-5 to achieve the 10% conversion. Extrapolating the HALPO-5 activity to the lower temperature indicates that HZSM-5 is three orders of magnitude more active than HALPO-5.
Catalyst Comparison
Temperature Required to Achieve 10% Conversion
to Xylenes Over 0.3 grams Catalyst
At Atmospheric Pressure
2 Microliter o-Xylene Pulses at 20 cc/min

Figure 44
Xylene Disproportionation

A xylene disproportionation mechanism (36,106) is depicted in Figure 45. The first step involves removal of a hydride from a methyl group on the xylene molecule, resulting in a benzylic carbenium ion. This cation attacks another xylene molecule at the aromatic ring. The diphenylmethane is then attacked by a proton at one of its aromatic rings. The resulting cation splits with the formation of toluene and a trimethylbenzene.

Since all of the steps are reversible (as indicated by Table 12), it is possible that under the appropriate conditions xylene isomerization will occur via these steps also. A suitable condition is that of the trimethylbenzene cation attacking a position different from the one it was formed from. The methyl group on an aromatic ring activates positions ortho and para to it due to its electron releasing ability. Thus, those two positions on the toluene molecule have equal probabilities of getting attacked.

Low levels of Lewis sites were expected for HSAPO-5. However, a Lewis site is required for disproportionation since that mechanism involves the abstraction of a hydride ion. Thus, a small number of the active sites could have been Lewis in nature.

Evidence for the proposed disproportionation mechanism is obtained from the deuterium label experiments in which the isomerized products show more exchange than the
Xylene Disproportionation Mechanism
(Ref. 36, 106)
Figure 45
reactants (pp. 119-121). A statistical distribution of the o-xylene aryl hydrogens is seen over wide ranges of carrier flowrates and reactor temperatures (Table 14). Additionally, from Table 5 it can be seen that only the aryl hydrogens of the cumene exchange. Based on the xylene isomerization mechanism, it is logical to presume that after a molecule has been isomerized at reaction conditions, it should re-scramble only its aryl hydrogens again into a statistical distribution before leaving the catalyst. There should not be a difference in $\phi$ values for the product and reactant xylene molecules. Figures 41 and 42, however, indicate that there was a difference over a wide range of conversions (10-70%).

Figure 44 indicates that a hydrogen is removed from (and later added to) a methyl group during disproportionation. Figure 39 indicates that a very small amount of isomerization occurs via disproportionation. Thus, a statistical distribution among the methyl hydrogens should not be seen. Also, a $\Delta \phi$ is possible for isomerization occurring through that route. Furthermore, the resulting difference should be lower for a catalyst that exhibits lower disproportionation activity. With its lower pore dimensions, HZSM-5 displays a lower $\Delta \phi$ than HSPO-5.

The major trimethylbenzene product was pseudocumene or 1,2,4-trimethylbenzene (TMB). As mentioned in the introduction, a statistical substitution of a third methyl group
into a meta-xylene ring would result in a 1,2,3:1,2,4,-TMB ratio of 1:2. For ortho-xylene, the ratio would be 1:1. Neither of these ratios was seen in the data. This is a direct result of catalyst's shape selectivity favoring the production of the smaller trimethylbenzene. Also, monomolecular isomerization has a higher activation energy than bimolecular isomerization. Furthermore, activation energies of bimolecular isomerization and disproportionation are similar. Thus, the low formation of transalkylation products in xylene isomerization is caused by shape selective, rather than thermodynamic, effects over HSAPO-5.

The value for the disproportionation activation energy over HSAPO-5 (8.5 kcal/mol) was higher than the 6.4 kcal/mol found by Gendy and Pratt (37) over an HY zeolite. However, it is lower than the 17.7 kcal/mol found by Hanson and Engel (22) over an amorphous silica-alumina. The former used a model similar to equation 28. On the other hand, the latter modeled the disproportionation as an irreversible reaction with Langmuir-Hinshelwood kinetics.
V. Summary

Although HSAPO-5 is structurally different from any known zeolite, it possesses many of the properties associated with them. It has a high exchangeable hydrogen concentration on the surface \((3.3 \times 10^{20} \text{ H-atom/gm})\) capable of isomerizing xylenes. These active sites for xylene isomerization on HSAPO-5 are presumed to be Brønsted in nature.

Its micropore diameter (8Å) does not exert shape selective effects on the xylene molecules (7-7.6Å) during isomerization (Figure 37). However, HSAPO-5 does limit (Tables 20 and 21) the transalkylation reaction due to the prevention of the formation of the bulky trimethylbenzenes (7.6-8.6Å) by its transition state selectivity.

HSAPO-5 undergoes deactivation and requires periodic regeneration. Under the time on stream deactivation model, the rate of activity loss decreases with temperature for short times on stream. Through regeneration, complete restoration of surface area and exchangeable hydrogen density is possible.

A model utilizing first order kinetics with respect to the reacting xylenes fits the CSTR initial rate data quite well. The difference in activation energies for m→p (24.4 \(\text{kcal/mol}\)) and m→o (21.4 \(\text{kcal/mol}\)) indicate that the former would be favored at higher temperatures (Figure 37). Low amounts of disproportionation products were observed. A bulk model for
the overall reaction led to an activation energy of 8.5 kcal/mole for the transalkylation process.

A related objective was to compare the catalytic activity of HSAP-5 with HZSM-5, HAIPO-5, and Houdry M-46. The series of catalysts had varying surface areas (Table 4), exchangeable hydrogen concentrations (Table 6), and xylene isomerization activities (Figure 44). Yet, an intramolecular (with respect to the methyl groups) xylene isomerization mechanism was clearly seen over all of the catalysts from the $^{13}$C experiments (Figure 39).
Appendix A

Tracer Experiments

To determine the flow behavior of the recycle flow system, a tracer study was conducted. Both step and impulse inputs were considered.

A plug flow with recycle reactor is a plug flow reactor that has a portion of its downstream flow diverted upstream of the reactor. \( R \), the recycle ratio, is the ratio of the volumetric flowrate of the recycle stream to the outlet stream from the reaction system. The analysis in Appendix C verifies that the appropriate conditions exist for this model to be valid.

For a step change in the input, the concentration history in the effluent is

\[
C_i = 1 - \left( \frac{R}{R+1} \right)^i \tag{A1}
\]

In Equation A1, \( i \) is \( \frac{t}{\tau} \) and \( \tau \) is the mean residence time in the plug flow portion. If \( R \) is large enough, the following approximation can be made

\[
\left( \frac{R}{R+1} \right)^i \approx \exp\left( \frac{-t}{\tau} \right) = \exp\left( \frac{-t}{\tau} \right) \tag{A2}
\]

where \( \tau \) is the space time for the "CSTR" reactor. Equation A1 becomes

\[
C(t) = 1 - \exp\left( \frac{-t}{\tau} \right) \tag{A3}
\]

The impulse response can be obtained from Equation A3 by
differentiation.

Under system pressures, the recycle ratio was 85. As is evident from Figure 46, R was large enough for the approximation to be made in Equation A2. Note that the impulse response can be used to make an accurate determination of the CSTR system volume. Calculated this way, the system volume was 36 cm$^2$. 
Figure 46
(Not to scale)
Appendix B

Reaction-Mass Balance Equation

The equation applied to the reaction system was

\[-r_a = \frac{P^0 - P}{\tau}\]  \hspace{1cm} (A4)

where \(\tau = \frac{V_T T_{ref}}{V_t}\), \(r_a\) is the reaction rate, \(P^0\) is the feed partial pressure, \(P\) is the partial pressure evident at the reactor steady state conditions, \(V_T\) is the volume of the reactor, \(T_{ref}\) is a reference temperature, \(R\) is the gas constant, and \(V_t\) is the volumetric flowrate.

This equation can be derived by starting with the typical steady state CSTR equation

\[-r_a = \frac{n^0 - n}{V_r}\]  \hspace{1cm} (A5)

where \(n^0\) is the feed molar flowrate and \(n\) is the molar flowrate at steady state.

Dividing by the total flowrate, \(V_t\), and assuming that the ideal gas law holds under the reaction system conditions, the following equations result

\[-r_a = \frac{C^0 - C}{\frac{V_r}{V_t}}\]  \hspace{1cm} (A6)
and \(-r_a = \frac{p^0 - p}{RT} \frac{V_T}{r_T \text{ref}} \frac{r_T}{V_T} \) \(\text{A7)}\)

where \(C^0 = \frac{n^0}{V_T} \) (the concentration of the feed).

Finally, Equation A4 is arrived at by canceling the \(T\)'s. Since the reactor was operated at a low pressure (slightly above atmospheric) and at high temperatures, the assumption of ideality in the vapor phase is reasonable.
Appendix C

Flow Regime for Reactor

The reaction-mass balance equation applied to the reaction system was developed for a CSTR system. The CSTR approximation was developed from preliminary modeling of the system as a plug flow with recycle reactor. To confirm the plug flow behavior in the reaction zone, two analyses were made.

Sternberg et al. (107) state that the diameter of the reactor should be at least ten particle diameters wide to remove wall effects and ensure a flat velocity profile. Considering a particle diameter of 0.45 mm and a reactor diameter was 10.2 mm, the criterion is fulfilled since the reactor is 23 particle diameters wide.

As a second test of the plug flow behavior, a check on the flow regime in the catalyst bed was made through the modified Reynolds number, $N'_{Re}$. It is defined (108) as follows

$$N'_{Re} = \frac{D_p G}{\mu}$$

where $D_p =$ average particle diameter
$\mu =$ fluid viscosity
$G =$ fluid superficial velocity, based
on empty chamber cross section
A modified Reynolds number less than 10 indicates non-turbulent flow.

The diameter of the plug flow portion is 0.41 in. Also, the maximum flow through the MB 41HT pump at system pressures is 0.17 ft\(^3\) (std) min\(^{-1}\). Thus, \(G_{\text{max}}\) is 0.0168 gram s\(^{-1}\) cm\(^2\). For helium, \(\mu_{\text{He}}\) is 299.2 \(\mu\)Poise at 282°C (109). Using this value, \(N_{\text{Re}}\) was 2.5. Thus, both of the checks confirmed the plug flow behavior through the reactor.
Appendix D

Effect of Diffusion on the Kinetics

The Weisz-Hicks criterion (108) was used to check if diffusion of the species influenced the reaction rate. It is defined as

\[
\Phi = \frac{R^2 \rho_p k_h}{D_{\text{eff}} \rho_b} \tag{A8}
\]

and

\[
\Phi = \frac{3\phi_s}{\tanh(\phi_s)} - 3 \tag{A9}
\]

and

\[
\eta = \frac{3}{\phi_s} \frac{\tanh(\phi_s)}{\phi_s} \tag{A10}
\]

where \( \Phi \) = the modified Thiele modulus, \( \eta \phi_s^2 \)

\( R \) = the particle radius, mm

\( D_{\text{eff}} \) = the effective diffusivity, \( \frac{cm^2}{s} \)

\( \rho_p \) = the catalyst particle density, \( \frac{g}{cm^3} \)

\( \rho_b \) = the catalyst bulk density, \( \frac{g}{cm^3} \)

\( \phi_s \) = the Thiele modulus

\( \eta \) = the effectiveness factor

\( k_h \) = first order rate constant, \( s^{-1} \)

Equation A10 holds for a spherical catalyst particle and first order kinetics. The effectiveness factor is defined as the ratio of the observed reaction rate to the diffusion-free reaction rate.
In order to check for diffusional limitations at both low and high reaction rates, the value of the modulus at low (350°C) and high (430°C) temperatures was checked. The catalyst particles were 30-50 mesh; thus, the particle radius, \( R \), was 0.225 mm. The catalyst densities were estimated from other porous solid acid catalysts \((110)\); \( \rho_p \) and \( \rho_b \) were 2 and \( 1 \frac{\text{g}}{\text{cm}^3} \), respectively. For a typical kinetic run, \( \tau \) was 29 seconds.

\( D_{\text{eff}} \) was estimated from the cumene cracking data over silica-alumina \((110)\). This is a reasonable estimation since cumene and xylenes are similar in size. Furthermore, since \( D_{\text{eff}} \) appears in the denominator and xylenes are smaller molecules, the true and greater \( D_{\text{eff}} \) for the xylenes would cause the following \( \Phi \) values to be lower. This would not change the conclusions. At 420°C, \( D_{\text{eff}} \) was \( 1.2 \times 10^{-3} \frac{\text{cm}^2}{\text{s}} \). The temperature dependence of \( D_{\text{eff}} \) was modeled as

\[
D_{\text{eff}}(T) = D_{\text{eff}}(T^*) \cdot \left( \frac{T^*}{T} \right)^{3/2}.
\]

For a first order reaction in a CSTR,

\[
k_h (\text{s}^{-1}) = \frac{X}{(1-X) \cdot \tau}
\]

At \( T = 350°C \), the following result

\[
\begin{align*}
&\circ \ D_{\text{eff}} = 1.023 \times 10^{-3} \frac{\text{cm}^2}{\text{s}} \\
&\circ \ X = 0.09
\end{align*}
\]
\begin{align*}
  & k_h = 3.35 \times 10^{-1} \text{ s}^{-1} \\
  & \phi = 0.0004 \\
  & \phi_s = 0.064 \\
  & \eta = 0.999
\end{align*}

At $T = 430^\circ\text{C}$, the following result
\begin{align*}
  & D_{\text{eff}} = 1.23 \times 10^{-3} \text{ cm}^2 \text{s}^{-1} \\
  & \chi = 0.50 \\
  & k_h = 33.9 \times 10^{-1} \text{ s}^{-1} \\
  & \phi = 0.034 \\
  & \phi_s = 0.185 \\
  & \eta = 0.998
\end{align*}

Thus, in the temperature range of the experiments, diffusion did not influence the reaction rate.
Appendix E

Calculation of $\Sigma_\omega$ and Improvement of Previous Method

The raw data collected from the $d_6$- and $d_0$-Benzene hydrogen exchange reactions were corrected for $^{13}C$ impurities. For the $i$th pulse, $\phi_i$ was defined to be the number of exchanged $^{13}C$ atoms per molecule. For exchange with $d_6$-Benzene, the following definition holds:

$$\phi_j = \sum_{i=0}^{6} (6-i)d_i$$  \hspace{1cm} (A11)

where $d_i$ is the mole fraction of the isomer with $i$ D atoms in the benzene ring. Calculated from the mass spectra, $d_i$ is the $i$th m/e peak height fraction.

For the $d_0$-Benzene exchange reactions,

$$\phi_j = \sum_{i=0}^{6} i d_i$$  \hspace{1cm} (A12)

$\Sigma_\omega$ is defined as the total number of hydrogens on the surface, i.e.

$$\Sigma_\omega = \sum_{j=1}^{\infty} \phi_j n_{bz}$$  \hspace{1cm} (A13)

where $n_{bz}$ is the number of Benzene molecules per pulse.

Since it was impossible to collect and analyze an infinite number of pulses, an extrapolation technique was followed. The scaling variable $P_j$ is defined as follows.
\[ P_j = \frac{6 - \phi_j}{6} \quad \text{(A14)} \]

Intuitively, \( P_j \) is bounded by 0 and 1. Figure 47 is an example of this plotting technique. In the figure, \( \left( \frac{1}{6} - 1 \right) \) is plotted versus \( \frac{1}{j} \). Thus, the \( y \)-intercept is 0. The value of \( P_j \) at \( j = \infty \) is an additional benefit of this procedure since the number of points to fit is one more than the number of data points.

The extrapolation method consists of fitting the data points to a curve that satisfies three requirements, i.e. the \( y \)-intercept is 0, the slope at the intercept is 0, and the curve is concave upwards. An example of this curve fitting technique is shown in Figure 47 where six sets of pulse experiments have been interpolated to calculate \( \Sigma_\infty \). After the appropriate curve is found, \( \phi_j \) is then calculated beyond the experimental number of pulses by using equation A14. Then the \( \Sigma_\infty \) sum of equation A13 is carried out. The extrapolation is continued until the successive changes in the sum are minimal, i.e. a change of less than 0.1%.

A comparison of this technique with one applied previously in this lab can be seen on Figure 48. Previously, the six points were extrapolated to the \( y \)-axis by performing a linear least squares fit. The accuracy of the fit dropped at the higher pulse numbers since there was a definite curvature. Note that the latter method results in values of \( \Sigma_\infty \).
Scaled Variable Curve Fitting

\[ y(0) = 0. \]
\[ y'(0) = 0. \]
\[ y''(0) \geq 0. \]

Figure 47
Comparison of Least Squares Extrapolation

to Scaled Variable Extrapolation for

Hydrogen/Deuterium Exchange

Figure 48
that are larger than those predicted by the extrapolation of the scaling technique.

Another improvement to the extrapolation procedure applied in this lab involves the analysis of cumene pulses over the acid catalyst (to recover the deuteriums left by the d₆-pulses). Benzene, instead of cumene, is caught and analyzed. Then the number of hydrogen atoms exchanged per cumene pulse, Σ, is found by multiplying by two the product of the φ calculated from the benzene analysis and nₜₖ, the number of benzene molecules per pulse. This is done since cumene has twice as many hydrogens as benzene.

It is evident from the results of this study that not all of the cumene hydrogens are equivalent. Only the aryl hydrogens readily exchange. Thus, the factor of two is erroneous. A more accurate adjustment of the benzene φ value (to obtain the cumene φ value) is necessary.

Cumene dealkylation can be written as follows

Cumene → Benzene + Propylene

or

A → B + C

If \( N'_a \) is the starting mole flowrate, concentration, etc., then the conversion is

\[
X = \frac{N'_a - N_a}{N_a}
\]  

A15)
Performing a stoichiometric analysis on the reaction, the number of cumene, benzene, and propylene molecules per pulse remaining after the reaction are

\[ N_a^0 = N_a (1 - X) \]  
\[ N_b^0 = N_a X \]  
\[ N_c^0 = N_a X \]

The acid catalyzed mechanism of cumene cracking involves the protonation of the benzene ring and the elimination of the alkyl side chain (103). Thus, it is reasonable to assume that propylene undergoes exchange to a statistical distribution of its hydrogens, which results in a \( \phi \) of 3. The total hydrogens exchanged per cumene pulse, \( \Sigma \), is the sum of unreacted cumene deuteriums and benzene product deuteriums. Since the alkyl group activates the aryl hydrogens, it is reasonable to assume that cumene exchanges to a statistical distribution over the aryl hydrogens only, i.e. \( \phi_{\text{cumene}} \) is 2.5.

Thus,

\[ \Sigma = N_a \cdot 2.5 + N_b \cdot \phi_{bz} + N_c \cdot 3 \]  

or

\[ \Sigma = ((1-X) \cdot 2.5 + X \cdot \phi_{bz} + 3 \cdot X) \cdot N_a \]  

or
\[ \Sigma = (2.5 + X(\phi_{bz} + 0.5)) \cdot N_{\text{cumene}} \]  

Although the conversion is necessary, the value for \( \Sigma \) calculated by equation A21 should be closer to the value calculated from the \( d_6 \)-benzene exchange results.
Appendix F

Linearity of Detectors

Several tests were run on the TCD and FID detectors to ensure that they were operated linearly. This was necessary to allow the use of calibration response factors for the calculation of mole and mass fractions. The responses from the detectors in the test were in the range of the experimental responses.

As seen in Table 19, the calculated CO₂ mole fractions equalled the measured mole fractions. Thus, the TCD detector behaved linearly. From Table 20, it is evident that the FID detector also behaved linearly.

Table 19

FID Linearity

<table>
<thead>
<tr>
<th>Injection Amounts</th>
<th>Calibration Areas*10^8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 µl</td>
</tr>
<tr>
<td>Mixture 5404</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.81</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.74</td>
</tr>
<tr>
<td>p-xylene</td>
<td>2.64</td>
</tr>
<tr>
<td>m-xylene</td>
<td>2.73</td>
</tr>
<tr>
<td>o-xylene</td>
<td>2.70</td>
</tr>
<tr>
<td>Mixture 5406</td>
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</tr>
<tr>
<td>Mesitylene</td>
<td>2.57</td>
</tr>
<tr>
<td>Pseudocumene</td>
<td>3.04</td>
</tr>
<tr>
<td>Hemellitene</td>
<td>2.98</td>
</tr>
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</table>
Table 20

TCD Linearity

CO₂ Mole Fraction

<table>
<thead>
<tr>
<th>Case</th>
<th>Measured¹</th>
<th>Calculated²</th>
</tr>
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<td>0.110</td>
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<td>2</td>
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<td>0.057</td>
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<tr>
<td>3</td>
<td>0.056</td>
<td>0.050</td>
</tr>
<tr>
<td>4</td>
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<td>0.049</td>
</tr>
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</table>

Notes:

¹ Using bubble flowmeter
² Using calibration constants
Appendix G

Initial Conversion Data Tables

Table 21
Meta-Xylene Feed Over HSAPO-5

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Toluene</th>
<th>Xylenes</th>
<th>Trimethylbenzenes</th>
<th>C. Wt. (qm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Para</td>
<td>Meta</td>
<td>Ortho</td>
</tr>
<tr>
<td>Feed 12.6 Torr</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>321</td>
<td>0.08</td>
<td>0.16</td>
<td>11.70</td>
<td>0.49</td>
</tr>
<tr>
<td>324</td>
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<td>0.18</td>
<td>11.74</td>
<td>0.39</td>
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<td>346</td>
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<td>11.38</td>
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<tr>
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<td>11.72</td>
<td>0.64</td>
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<tr>
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<td>9.99</td>
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<td>3.55</td>
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Table 22
Ortho-Xylene Feed Over HSAPO-5

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<tr>
<th>Feed (torr)</th>
<th>Temp (°C)</th>
<th>Toluene</th>
<th>Para</th>
<th>Meta</th>
<th>Ortho</th>
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<th>P</th>
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References


89. Lok, B. M., Markus, B. K., and Angell. C. L., Zeolites, 6 185 (1986).


