ABSTRACTS

THE FIRST NORTH AMERICAN MEETING

OF

THE CATALYSIS SOCIETY

THE TRAYMORE HOTEL
ATLANTIC CITY, NEW JERSEY
FEBRUARY 20-21-22, 1969
PROGRAM

THE FIRST NORTH AMERICAN MEETING OF THE CATALYSIS SOCIETY

J. H. Sinfelt, Program Chairman

Thursday, February 20, 1969

9:00-9:15 Opening Remarks -- F. G. Ciapetta

Symposium on Kinetic and Mechanistic Studies of Catalytic Reactions
J. H. Sinfelt, Presiding

9:15-9:45 Catalytic Hydrogen Transfer Between Cyclohexane and Benzene on Supported Metals -- G. Parravano

9:45-10:15 Reaction Rate Modeling Utilizing Stoichiometric Number Concept -- John Happel, Miquel A. Hnatow, and Reiji Mezaki

10:15-10:45 The Mechanism of Carbon Monoxide Oxidation over Silver -- George W. Keulks, Charles C. Chang, and Frederic C. Wilhelm

10:45-11:15 Catalytic Decomposition of Hydrogen Peroxide by Metals and Alloys of the Platinum Group -- D. W. McKee


11:45-12:15 Hydrogenolysis of Alcohols. II. Reduced Nickel Oxide -- Its Intrinsic Acidity and Catalytic Activity in the Conversion of Alcohols to Ethers -- Herman Pines and Tad P. Kobylniski

12:15-1:30 Lunch

1:30-2:00 Different Mechanisms of Aromatization of Trimethylpentanes Over Chromia-Alumina and Platinum-Alumina Catalysts -- G. R. Lester

2:00-2:30 Olefin Disproportionation Catalysts and Reactions -- R. L. Banks, G. C. Bailey, L. F. Heckelsberg, and F. Pennella

2:30-3:00 Stereochemistry of the Catalytic Hydrogenation of 2-Aryl-bicyclo (2.2.1) Heptane Derivatives -- Fabian T. Fang, and Frank L. Slejko

3:00-3:30 Transient Intermediates in SbF₅/HSO₃F -- G. M. Kramer

3:30-4:00 Metal Complexes of Phthalocyanine and α, β, γ,δ-Tetraphenylporphyrin as Heterogeneous Catalysts in Oxidative Dehydrogenation -- Joost Manassen and Amiram Bar-Ilan

4:00-4:30 Hydroformylation Catalysis by Arylphosphine Complexes of Rhodium -- J. H. Craddock, A. Hershman, F. E. Paulik, K. K. Robinson, and J. F. Roth

4:30-5:00 Supported Liquid-Phase Catalysts -- Peter R. Rony
Symposium on Surface Chemistry and Adsorption on Catalysts

D. J. C. Yates, Presiding

9:00-9:30 Use of Temperature Programmed Desorption To Study The Development of Active Sites in Oxide Catalysts -- Y. Amenomiya and R. J. Cvetanovic

9:30-10:00 The Exchange of H$_2$O$^{18}$ with the Oxygen of Promoters on The Surface of Iron Synthetic Ammonia Catalysts -- V. Solbakken, A. Solbakken, and P. H. Emmett

10:00-10:30 Copper Oxide Supported on Alumina. III. X-Ray K-Absorption Edge Studies of the Cu$^{+2}$ Species. Alexander Wolberg and James F. Roth

10:30-11:00 Adsorption Studies Using Mossbauer Spectroscopy -- M. C. Hobson, Jr. and H. M. Gager

11:00-11:30 Adsorption of Oxygen and Hydrogen on Platinum. Part I. Unsupported Metal -- M. A. Vannice, J. E. Benson, and M. Boudart

11:30-12:00 The Adsorption of Nitric Oxide on Chromia-Alumina -- K. Otto and M. Shelef

12:00-1:30 Lunch

1:30-2:00 Surface Species on Vanadium -- George Blyholder and Marvin C. Allen

2:00-2:30 Perturbation of Surface Hydroxyl Groups on Porous Vycor Glass by Aromatic $\pi$-Electron Systems -- J. A. Cusumano and M. J. D. Low

2:30-3:00 The Pore Geometry of Raney Nickel -- J. Freel, W. J. M. Pieters, and R. B. Anderson

3:00-3:30 Disproportionation of Carbon Monoxide over Iron and Silicon-Iron Single Crystals -- C. Roscoe, and P. L. Walker, Jr.

3:30-4:00 Production, Properties and Reaction of Metallic Sodium Films in Porous Vycor Glass -- John Turkevich and Toshio Sato

4:00-4:30 Selectivity and Stoichiometry of Copper Oxide in Propylene Oxidation -- B. J. Wood, H. Wise, and R. S. Yolles

4:30-5:00 Studies of the Hydrogen Held by Solids XVII. The Ortho-Para Hydrogen Conversion and Hydrogen-Deuterium Exchange Reactions over a Transition Al$_2$O$_3$ -- F. H. van Cauwelaert and W. Keith Hall.
Saturday, February 22, 1969

Symposium on Molecular Sieves

J. A. Rabo, Presiding

9:00- 9:30  Relative Activities of Crystalline and Amorphous Aluminosilicates -- Rowland C. Hansford and John W. Ward

9:30-10:00  The Isomerization of the Xylenes Using Zeolite Catalysts -- M. A. Lanewala and A. P. Bolton

10:00-10:30  Catalytic Properties of Hydroxyl Rich and Dehydroxylated LaY -- J. A. Rabo and C. L. Angell

10:30-11:00  Quinoline Titrations for Cumene Cracking Activity on Molecular Sieve Catalysts -- M. S. Goldstein and T. R. Morgan

11:00-11:30  An EPR Study of Crystal Field Interactions on Group IIA-Y Zeolites -- Jack H. Lunsford and Katherine M. Wang

11:30-12:00  Studies of the Catalytic Dealkylation of Ethyl Acetate -- S. K. Sanyal and S. W. Weller

12:00-12:30  Thermal Behavior of Faujasite -- W. J. Ambs and W. H. Flank
Catalytic Hydrogen Transfer
Between Cyclohexane and Benzene
on Supported Metals

by

G. Parravano,
Department of Chemical and Metallurgical Engineering
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Ann Arbor, Michigan

It has been found that the transfer of hydrogen between cyclohexane and benzene occurs readily in the presence of supported metal catalysts. The reaction is easily studied by employing isotopically tagged benzene, namely:

\[ {^*C_6}H_6(g) + C_6H_{12}(g) \rightarrow C_6H_6(g) + {^*C_6}H_{12}(g) \]  \( 1 \)

where \(^*C\) is an isotopically tagged carbon atom. The experiments were conducted by flowing a mixture of benzene and cyclohexane, containing radioactive benzene, in a stream of purified \( \text{He} \) over a fixed catalytic bed. The reactor outlet was fractionated by gas chromatography, the fractions collected by freezing at liquid \( \text{N}_2 \) temperature and analyzed by liquid scintillation counting techniques. The variables investigated and their range were:
- \( [C_6H_{12}]/[C_6H_6] \) ratio, 0.02 to 220; temperature 80 to 140\(^\circ\)C;
- additions of up to 5% vol. of \( \text{H}_2 \) to the reacting mixture. The metals studied include: Pt, Rh, Ir, Ru, Pd. All metals were supported on high area alumina at the concentration of 0.7% weight. For Pt the influence of the concentration of the metal was investigated between 0.3 and 5% weight.

During the occurrence of reaction (1) a chemical equilibrium between gas and surface, invariant in the reactor space and time, is established. The chemical potential of the intermediate of reaction (1), adsorbed hydrogen, is a function of the ratio \( [C_6H_{12}]/[C_6H_6] \) at equilibrium. This ratio is constant and known during reaction (1). Thus, by obtaining experimental results at various \( [C_6H_{12}]/[C_6H_6] \) ratios, the influence of the chemical potential of adsorbed hydrogen upon the rate of transfer can be determined. The experimental results are discussed in this light and the influence of the catalytic variables of the system upon the chemical potential of adsorbed hydrogen and of the transfer rate is deduced. From this information interesting conclusions upon
the mechanism of hydrogen transfer and, particularly, upon the nature of the surface transfer centers, are obtained. Similarly, the results on the influence of molecular \( \text{H}_2 \) upon the rate of reaction (1) are advantageously employed to infer the limiting stage of the rate of the catalytic hydrogenation of benzene.

Since adsorbed hydrogen is the intermediate in the catalytic hydrogenation of aromatics, it is shown how reaction (1) represents a useful and interesting kinetic tool for the study and classification of catalyst behavior in the hydrogenation of aromatic hydrocarbons.
REACTION RATE MODELING UTILIZING STOICHIOMETRIC NUMBER CONCEPT

John Happel and Miguel A. Hnatow - The Department of Chemical Engineering
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Reiji Mezaki - The Department of Engineering and Applied Science
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Abstract

The stoichiometric number concept introduced by Horiuti is employed to develop a generalized rate expression applicable to situations with one or more rate controlling steps. The utilization of this concept provides the precise formulation of a potential term of the rate expression and thus simplifies greatly the modeling of a reaction rate equation. The use of this concept is of value for the analysis of reaction rate data which is obtained for a wide spectrum of experimental conditions. In order to illustrate the use of this method of modeling, the system involving vapor phase catalytic dehydrogenation and hydrogenation of butane -butenes on a commercial grade chromia-alumina catalyst was studied. Experiments were conducted using a differential flow type reactor under varying temperatures, from 400 to 560°C, and total pressures, from 0.1 to 1.0 atm.

An earlier investigation using carbon-14 tagged butane and 1-butene showed that the stoichiometric number of this reaction system is unity. This implies that a single step whose stoichiometric number of unity is controlling or that two or more rate controlling steps may be controlling each with a stoichiometric number of unity. Regardless of the nature of the rate controlling step or steps, the stoichiometric number determines clearly the potential term of the rate equation model

\[ r = \phi \left( p_{\text{Butane}} - \frac{p_{\text{Butenes}}}{p_{\text{H}_2}} \frac{p_{\text{H}_2}}{K_{eq}} \right) \]

where \( \phi \) is a function which contains rate parameters and the partial pressures of various reaction components and \( K_{eq} \) is the thermodynamic equilibrium constant of the reacting system.
In order to define the function \( \varphi \), several traditional rate models were employed in this study. It was found, however, that no models derived on the assumption of a uniform surface with non-interacting sites would correlate both the dehydrogenation and hydrogenation data simultaneously. Therefore several new models were developed and were tested by the statistical techniques such as the examination of the residuals of rate and the exploration of the confidence regions of parameter estimates. All constants were estimated through non-linear regression technique. The one which seems to represent approximately eighty data points best is the following rate equation

\[
r = \left[ \frac{\alpha \, P^n_{\text{Butane}}}{1 + K_{\text{Butane}} \, P_{\text{Butane}}} \, \frac{1}{n+1} + \frac{\beta \, P^n_{\text{Butenes}}}{1 + K_{\text{Butenes}} \, P_{\text{Butenes}}} \, \frac{1}{n+1} \right] \left( \frac{P_{\text{Butane}}}{K_{\text{eq}}} - \frac{P_{\text{Butenes}}}{K_{\text{H2}}} \right)
\]

where \( \alpha \) and \( \beta \) are, respectively, the forward reaction rate constants for the dehydrogenation and hydrogenation reaction and \( K_{\text{Butane}} \) and \( K_{\text{Butenes}} \) denote, respectively, the adsorption equilibrium constants of butane and butenes. \( n \) is an empirical constant and is larger than unity. Preliminary correlation on the basis of simple power law kinetic relationships indicated that hydrogen does not effect the dehydrogenation rate and is first order power for the hydrogenation rate. For the dehydrogenation of saturated hydrocarbons and the hydrogenation of unsaturated hydrocarbons, it is a general observation that the adsorption equilibrium constant of hydrogen is much smaller than those of hydrocarbons. On that ground the hydrogen term was not included in the denominator of the rate equation. The elimination of the term may also be considered logical in the light of parsimonious parameterization. The rate equation presented in this investigation must be regarded empirical. However it would be consistent with the assumption of non-uniform surface with two non-interacting different types of sites.
A number of metals and metal oxides are known to be active catalysts for the oxidation of carbon monoxide. On a number of these catalysts the mechanism for oxidation involves a surface carbonate intermediate. Published results on the oxidation over silver, on the other hand, suggest that the oxidation does not involve the surface carbonate intermediate.

To examine this possibility a detailed investigation of the mechanism of carbon monoxide oxidation over silver was undertaken. The silver catalysts used in this investigation were commercial silver powder and silver powder prepared from silver carbonate. All of the chemicals used in the catalyst preparation and the reactant gases were of high purity. The reaction was studied in a circulation system, and gold leaf traps were used throughout the system to protect the catalyst against mercury vapor. Normal catalyst pretreatment involved reduction at 300°C and outgassing at 300 - 500°C to a residual pressure of <10⁻⁶ torr. After the outgassing treatment, the catalyst temperature was lowered to 100°C under vacuum. The catalyst then was isolated from the rest of the system, and the desired gas mixture introduced into the system. The rate of the oxidation was followed by circulating the gas mixture over the catalyst and periodically analyzing the gas composition by a mass spectrometer.

When carbon dioxide was trapped from the gas mixture by liquid nitrogen, the reaction was found to be first order in carbon monoxide pressure and zero order in oxygen pressure. This kinetic rate law was determined by fitting the data to the integrated rate expression, as well as by varying the initial pressures of carbon monoxide and oxygen. When carbon dioxide was not trapped from the gas mixture, an inhibition of the rate was found. The data fit the integrated rate expression for the rate law corresponding to first order in carbon monoxide pressure, zero order in oxygen pressure, and negative first order in carbon dioxide pressure.

Experiments with pure oxygen-18 yielded pure CO₁₈O₁₈ when the carbon dioxide was trapped from the gas mixture. Without trapping, the carbon dioxide was found to rapidly equilibrate with the oxygen-18. In experiments with a mixture of oxygen-16 and oxygen-18, no equilibration of oxygen was detected.

These results are interpreted in terms of a mechanism in which oxygen is strongly and irreversibly chemisorbed on silver. The carbon monoxide reacts with the chemisorbed oxygen either by a collisional process from the gas phase or from a physically adsorbed layer. The mechanism of carbon dioxide equilibration is not entirely clear, but it appears that it may involve a carbonate intermediate.
Supplemental evidence for this mechanism has been provided by infrared and x-ray studies. Infrared studies on alumina and silica supported silver have revealed that carbon monoxide does not chemisorb on silver or silver oxide. Thus far carbon dioxide has not been found to chemisorb on the supported silver samples, but has been found to produce carbonate bands on silver oxide films. The x-ray diffraction studies have confirmed that silver carbonate is formed when silver oxide is exposed to carbon dioxide. No silver carbonate is detected by x-ray, however, when silver is exposed to carbon dioxide.

2180 cm⁻¹ absorption for CO on silver - weak & reversible

\[
\begin{align*}
\frac{1}{2} \text{CO}_2(g) & \rightarrow \text{CO(ads)} \\
\text{CO(g)} & \rightleftharpoons \text{CO(ads)} \\
\text{CO(ads)} + \text{O(ads)} & \rightarrow \text{CO}_2(ads) \\
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(ads)
\end{align*}
\]
CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY METALS AND ALLOYS OF THE PLATINUM GROUP

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Although the catalytic decomposition of aqueous hydrogen peroxide has often been studied on metals such as silver or platinum, few systematic studies have been carried out with alloy catalysts. The reaction is unusual in that electron transfer from the metal to the adsorbate appears to be involved, although the detailed mechanism is by no means established. Hydrogen peroxide is believed to be an intermediate in the electrochemical reduction of oxygen under certain conditions (1) and the ability to catalyze its decomposition is often used to test potential cathode materials for fuel cells and batteries (2).

The decomposition of dilute aqueous solutions of hydrogen peroxide has been studied on a range of metal and alloy catalysts of Groups VIII and IB. The finely powdered samples were prepared by reduction of mixed salt solutions by means of sodium borohydride. In most cases, the catalysts were homogeneous alloys of high surface area. Kinetic measurements were generally carried out at 27.0°C, using a method similar to that described by Keating, Rozner and Youngblood (3) and the activity of the alloys was studied as a function of catalyst composition, peroxide concentration and pH of the solution.

In neutral solution at 27.0°C, the activity of the individual metals of Group VIII$^3$ was generally greater than those of Group VIII$^2$, the order of specific activity (per unit surface area) decreasing in the sequence Pt > Os > Ir > Pd > Ru > Rh. Alloys of platinum-palladium, platinum-ruthenium and platinum-rhodium showed specific activities intermediate between those of the constituent metals. On the other hand, alloys of platinum-iridium, palladium-gold and palladium-silver showed maximum specific activities at certain intermediate alloy compositions. Alloys of platinum and iridium, containing 10-20 percent iridium, were the most active catalysts found, the rates of peroxide decomposition being diffusion limited under the conditions of the experiments. The maximum rate observed with a Pd-16% Au alloy corresponded to a 20-fold
increase over that found for pure palladium. A similar maximum was observed with the palladium-silver alloy series.

Although the reaction was generally first order at low peroxide concentrations, the kinetics depended strongly on the pH of the solutions, the decomposition being more rapid in basic than in acidic solutions. In every case the rate rose to a sharp maximum at pH values around 11 and decreased rapidly in stronger acid or alkaline solutions. With increasing gold content the activities of the alloys diminished rapidly with increasing acid strength.

Although the mechanism of the peroxide decomposition reaction can not be established unequivocally, the existence of an optimum hydrogen ion concentration is consistent with the Haber-Weiss chain mechanism (4). It is likely also that the formation of oxide films on the metal surface will result in a change in mechanism at high pH values.

Acknowledgment - Part of this work was performed under Contract No. DAAK 02-67-008 with the U.S. Army Mobility Equipment Research and Development Center, Ft. Belvoir, Virginia.

REFERENCES

KINETICS OF THE HYDROGENATION OF SOME TERT-BUTYL SUBSTITUTED BENZENES

By

Samuel Siegel and James F. Outlaw, Jr.

Department of Chemistry, University of Arkansas

The mechanism of the catalytic hydrogenation of the benzene ring is clarified by examining the kinetics of the reaction of a number of tert-butyl substituted benzenes (t-butyl-, 1,3-di-t-butyl-, and 1,4-di-t-butylbenzene and 4-t-butyltoluene) over an alumina supported rhodium catalyst. The rates of reduction of these compounds have the same dependence on the concentration of substrate (zero order) and pressure of hydrogen (first order) and increase in the sequence t-butyl-(1.00), 1,3-di-t-butyl-(1.03), 4-t-butyl-1-methyl-(1.38), and 1,4-di-t-butyl-(1.69). In competitive experiments the order of reactivity is t-butyl->4-t-butyl-1-methyl-> 1,3-di-t-butyl> 1,4-di-t-butylbenzene which, via a quantitative treatment of a conventional mechanistic scheme, for example see C. P. Rader and H. A. Smith, J. Am. Chem. Soc., 84, 1443 (1962), yields the relative adsorption coefficients of 1.0, 0.10, 0.02 and 0.01 respectively. Apparently the t-butyl-group tends to decrease the attraction between the aromatic ring and the catalytic site (smaller adsorption coefficient). Because the rate constants for the reduction of the adsorbed species increases as the strength of adsorption decreases, one may conclude that the substitution of a t-butyl-group for a hydrogen atom affects the energy of the transition state for the reduction to a much lesser extent than it increases the energy of the adsorbed aromatic hydrocarbon.

The hydrogenation of 1,4-di-t-butylbenzene is particularly instructive in that an unusually large amount of the intermediate cycloalkene, 1,4-di-t-butylcyclohexene, is formed. The concentration is large enough so that the kinetics of formation and disappearance can be readily determined and is represented approximately by the expression:
\[
\frac{d[\text{alkene}]}{dt} = S k_R [H_2] [B]^0 - k_E [H_2]^{1/2} [E]
\]

where \( S \) is the fraction of aromatic hydrocarbon \([B]\) which produces 1,4-di-\(t\)-butylcyclohexene, \([H_2]\) the pressure of hydrogen, and \([E]\) the concentration of the cycloalkene. \( S \) is approximately 0.75 so that about twenty-five percent of the reduction does not proceed via 1,4-di-\(t\)-butylcyclohexene. However, this may be the fraction which proceeds via an isomer such as \(\text{cis}\)-1,4-di-\(t\)-butylcyclohexene which would be expected to hydrogenate much more rapidly.

Qualitatively the reduction of 1,3-di-\(t\)-butylbenzene is similar although the maximum concentration of the intermediate cycloalkene is much less so that the kinetics of formation and disappearance of the intermediate is not easily measured. This we attribute to the slower rate of reduction of the aromatic hydrocarbon rather than to an increasingly important reaction path which bypasses the cycloalkene. The stereochemistry is consistent with this interpretation. (See S. Siegel, Advan. Catalysis 16, 123 (1966).)
Reduced Nickel Oxide - Its Intrinsic Acidity and Catalytic Activity in the Conversion of Alcohols

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It was reported previously from this laboratory that nickel-kieselguhr catalyst in the presence of hydrogen at atmospheric pressure and at temperatures of 150° to 190°, converts primary alcohols and diols, according to the following main reactions:

1. \[ \text{RCH}_2\text{CH}_2\text{OH} + 2\text{H}_2 \rightarrow \text{RCH}_3 + \text{CH}_4 + \text{H}_2\text{O} \]
2. \[ \text{RCH}_2\text{CH}_2\text{OH} + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_3 \text{ and } \text{R}^1\text{CH}_2\text{CH}_3 \]
3. \[ 2\text{RCH}_2\text{CH}_2\text{OH} \rightarrow (\text{RCH}_2\text{CH}_2)_2\text{O} \]

(\(\text{R}^1\) is the product of skeletal isomerization)

It has been proposed that reaction 1 proceeds through the decarbonylation of the intermediate aldehydes produced by the dehydrogenation of the alcohols. The reductive dehydroxylation and ether formation, equations 2 and 3 were considered to be acid catalyzed reactions. The methods of preparation of the nickel-kieselguhr catalysts can greatly influence the selectivity of the reaction.

The present paper describes the use of reduced nickel oxide as a catalyst for the conversion of primary alcohols, and the effect of its preparation on the selectivity of the products. The alcohols chosen for this study were n-butanol, 2-methyl-\(\cdot\), 3-methyl-\(\cdot\), and 3,3-dimethylbutanol (neopentyl alcohol).

The experiments were made in a micropulse reactor. Powdered nickel catalyst, 200 mg., was placed in the middle of the reactor tube, between layers of glass wool, and the rest of the reactor was filled with glass beads of 20-30 mesh size. The catalyst was prepared by precipitating nickel hydroxide from an aqueous solution of nickel nitrate with an excess of ammonium hydroxide, followed by drying and decomposing it to nickel oxide by heating in a flow of helium at 500° for four hours. The nickel oxide was then reduced to nickel in a flow of hydrogen.
For an optimum yield of ether the nickel catalyst must contain between 1.0 and 2.6% of nickel oxide. At 170° with a catalyst containing 2.1% nickel oxide the conversion of the alcohols amounted to 6 to 8% and the yield of dineopentyl ether and di-2-methyl-butyl ether were respectively 88 and 82%. When the nickel oxide content of the nickel catalyst was 0.05% the ether yields dropped to 5 and 18% respectively and the main reaction was reductive dehydroxymethylation (reaction 1).

The formation of ether was related to intrinsic acidic sites of the nickel-nickel oxide catalyst. The presence of 0.05% by weight of sodium ions in the catalyst reduces the yield of the ethers from about 78% to 5%. The reductive dehydroxymethylation becomes the main reaction.

In the absence of alkali metals and in the presence of a nickel catalyst containing 2.1% of nickel oxide, neopentyl alcohol formed besides dineopentyl ether, also small amounts of neopentane and 1,1-dimethylcyclopropane. The production of the former is explained by the hydrogenolysis of 1,1-dimethylcyclopropane. For the dimethylcyclopropane to be produced it is required that both intrinsic basic and acidic sites of the nickel-nickel oxide participate in the elimination of the elements of water.

Nickel is the first catalyst reported from this laboratory to convert neopentyl alcohol to dineopentyl ether. This ether prior to this study has not been reported in the literature and cannot be prepared by the conventional dehydrating catalysts.

The mechanism of the conversion of alcohols by nickel-nickel oxide catalyst will be discussed.
DIFFERENT MECHANISMS OF AROMATIZATION OF TRIMETHYLPENTANES OVER CHROMIA-ALUMINA AND PLATINUM-ALUMINA CATALYSTS

by

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The mechanism of the aromatization of trimethylpentanes over promoted and unpromoted Cr₂O₃-Al₂O₃ catalysts has been examined extensively by previous workers and the results of those studies often have been considered applicable to supported metal catalysts. The present work demonstrates that quite different mechanisms and reaction intermediates are involved in this reaction over an oxide-type catalyst on one hand and a supported metal catalyst on the other.

Although Herrington and Rideal originally proposed the existence of cyclopentane intermediates to explain their results over Cr₂O₃-Al₂O₃, Pines and others have concluded that on non-acidic Cr₂O₃-Al₂O₃ the reaction involves chain-lengthening of 1,5-diadsorbed pentanes via cyclopropyl or cyclobutyl intermediates and dehydrocyclization of the resultant 1,6-diadsorbed hexane. Some results with a base-promoted Cr₂O₃-Al₂O₃ are shown below and indicate that cyclopentanes are not important intermediates with such catalysts. This conclusion is based on the fact that although both 2,2,4-trimethylpentane and 2,4,4-trimethylpentene-2 yield para-xylene as the only C₈ aromatic, the only possible cyclopentyl intermediate, 1,1,3-trimethylcyclopentane, produces a C₈ mixture rich in meta-xylene.

<table>
<thead>
<tr>
<th>Feed</th>
<th>p-Xylene</th>
<th>m-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>100.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2,4,4-Trimethylpentene-2</td>
<td>100.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1,1,3-Trimethylcyclopentane</td>
<td>29.</td>
<td>64.</td>
<td>7.</td>
</tr>
</tbody>
</table>

We have found, however, that cyclopentanes are important intermediates when the paraffins are reacted with H₂ over base-promoted Pt-Al₂O₃. In the first place, considerable amounts of trimethylcyclopentanes were found in the product when trimethylpentanes were passed over this catalyst at 425°C. For example, 2,2,4-TMP showed up to about 35% conversion to 1,1,3-TMCP, while both 2,2,3-TMP and 2,3,3-TMP gave 25% of 1,1,2-TMCP; 2,3,4-TMP produced a similar quantity of the three geometric isomers of 1,2,3-TMCP. Secondly, each of the paraffins gave substantially the same C₈ aromatic distribution that the product cyclopentane produced when it was used as the feedstock. For example, both 2,2,4-TMP and 1,1,3-TMCP gave a 40-60 mixture of para and meta xylenes; 2,2,3-TMP, 2,3,3-TMP and 1,1,2-TMCP each gave 78% meta and 22% ortho xylenes; and 2,3,4-TMP, 1,cis-2, trans-3-TMCP and 1,trans-2, cis-3-TMCP each produced a mixture of 43% para, 43% ortho and 14% meta xylenes.

These results have led us to speculate that C₅ to C₆ ring enlargement on the basic Pt-Al₂O₃ occurs through electron deficient species adsorbed at platinum sites. This ring enlargement appears to be the rate-determining step in the aromatization reaction over this catalyst.
OLEFIN DISPROPORTIONATION CATALYSTS AND REACTIONS

by


Phillips Petroleum Company - Bartlesville, Oklahoma

Olefins disproportionate in a highly specific and efficient manner over a number of heterogeneous catalysts. Among the active disproportionation catalysts are tungsten oxide-silica which is effective above 300°C, molybdena-alumina which is effective in the 100 to 200°C range and rhenium oxide-alumina which is effective below 100°C.

Pretreatment of tungsten oxide-silica catalyst at about 600°C with hydrogen, carbon monoxide, or hydrocarbons improved the activity of the catalyst for disproportionating olefins. The hydrogen and hydrocarbon pretreatments also reduced double-bond isomerization activity of the catalyst which resulted in higher selectivities to primary disproportionation products. For example, over hydrogen-pretreated tungsten oxide-silica catalyst propylene was disproportionated at near equilibrium conversion (42 per cent) and 97 per cent selectivity to ethylene and 2-butene as compared to 32 per cent conversion and 92 per cent selectivity without the hydrogen pretreatment.

High selectivities to primary disproportionation products were also achieved by neutralizing the acid-type isomerization sites with sodium or potassium ions. Over a cobalt molybdate catalyst treated with potassium hydroxide, selectivities higher than 90 per cent were achieved in disproportionating 2-octene to 2-butene plus 6-dodecene and in disproportionating 3-heptene to 3-hexene and 4-octene. Without base-treatment of the catalyst selectivities were less than 25 per cent.

Although reduction in double-bond isomerization activity is preferred for certain applications, to disproportionate olefins such as 2-butene, high double-bond isomerization activity is needed. It was found that magnesium oxide, a very selective double-bond isomerization catalyst, was compatible with tungsten oxide-silica and could be activated under identical conditions. The conversion of 2-butene to disproportionation products over tungsten oxide-silica catalyst was increased from 27 per cent to 60 per cent by mixing magnesium oxide catalyst with the tungsten oxide-silica.

The disproportionation reaction is applicable to many olefins and combinations of olefins. The disproportionation of propylene, butenes, pentenes, heptenes, and octenes have been demonstrated. Isobutene disproportionates with itself to give dimethylbutenes and ethylene, with propylene to give methylbutene and ethylene, and with 2-butene to give methylbutene and propylene. These reactions are reversible, isobutene is obtained from 2,3-dimethylbutene and ethylene. Alpha-omega diolefins were produced when cyclic olefins were cleaved with ethylene; 1,6-heptadiene was obtained from cyclopentene and ethylene and 1,7-octadiene from cyclohexene and ethylene.
Dienes and acetylenes will also disproportionate. Butadiene was disproportionated to ethylene and cyclohexadiene, and butadiene plus propylene was converted to pentadiene and ethylene. Pentyne was disproportionated to 2-hexyne and 3-hexyne at 44 per cent conversion and 53 per cent selectivity.

The experimental results are consistent with a reaction mechanism involving the formation of a four-membered intermediate from the two interacting olefinic, or acetylenic, structures. The over-all process according to this mechanism involves the cleavage of two unsaturated bonds and the formation of two new unsaturated bonds.
"STEREOCHEMISTRY OF THE CATALYTIC HYDROGENATION OF 2-ARYLBICYCLO-
[2.2.1]HEPTANE DERIVATIVES"

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The stereochemistry of the catalytic hydrogenation of isomeric 2-anisyl-2-bornenes(I) and 2-anisyl-2-norbornenes(II), and the hydrogenolysis of the corresponding 2-anisyl-2β-bornanols(III) and 2-anisyl-2α-norbornanols(IV) was investigated for several reasons: (1) The reactant and product molecules possess rigid stereoconfigurations; (2) Product analyses by nuclear magnetic resonance spectroscopy and capillary gas chromatography had been established in a related study of solvated-electron reductions; (3) Any aryl substituent effects and a comparison of the hydrogenation and hydrogenolysis results would afford some insight of the intermediates and transition states involved; (4) Further saturation of the aromatic rings would yield novel cyclohexane derivatives for conformational analysis.

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{OCH}_3 & \quad \text{OCH}_3 & \quad \text{OCH}_3 \\
\end{align*}
\]

The hydrogenation of o-, m- and p- 2-anisyl-2-bornenes was studied using a palladium/carbon catalyst at low pressures and a Raney nickel catalyst at high pressures. With both catalysts the preferred products were the less stable exo-anisylbornanes. Much greater selectivity was found with the Raney nickel catalyst.

The stereoselectivity of these reactions may be explained in terms of the more stable intermediate structure formed as the reactant molecule is adsorbed on the catalyst surface. Here the addition of hydrogen from the least hindered side of the bridged bicyclic system would give the less stable isomer. Under the conditions of the nickel catalysis, the substrate is more strongly bonded to the catalyst surface. This causes the less stable intermediate to be even more sterically hindered, and results in the formation of much smaller amounts of the more stable endo-anisyl isomer.

Similar hydrogenations of the 2-anisyl-2-norbornenes over the palladium/carbon catalyst gave, in this case, the less stable endo-anisylnorbornanes exclusively. The complete stereoselectivity here is consistent with the so-called "exo-addition rule" for reactions of norbornene derivatives.
Hydrogenation of the 2-anisyl-2-bornenes for extended periods of time over W-5 Raney nickel resulted in the saturation of the aromatic ring. The meta and para compounds gave non-equilibrium mixtures of the cis- and trans-2β-(methoxycyclohexyl)bornanes and also 2β-cyclohexylbornane in apparently kinetically-controlled processes. The irreversibility of these hydrogenations may be explained in terms of a high energy barrier encountered in the dehydrogenation step which would involve a vinyl ether intermediate.

On the other hand, hydrogenation of the corresponding phenol derivatives (prepared by demethylation of the anisyl compounds) under similar conditions was found to yield equilibrium mixtures of cyclohexanol derivatives. In this case, the activation energy leading to the transition state of the reverse reaction, which now involves a ketone intermediate, should be considerably lower. The reaction conditions apparently allowed dehydrogenation of the cyclohexanols to take place on the nickel catalyst surface.

Analogous hydrogenation of 2-o-anisyl-2-bornene afforded a mixture of cis- and trans-2β-(2-methoxycyclohexyl)bornanes, 2β-cyclohexylbornane, as well as cis- and trans-1-(2-methoxycyclohexyl)camphanes and 1-cyclohexylcamphane, the skeletal rearrangement products. These results support the belief that, in the adsorbed intermediate species, a partial positive charge is developed on the C-2 atom. The nearby methoxyl group in the ortho compound would intensify the positive charge, causing a shift of the 1,6-bonding electron pair to yield the camphane derivatives.

Hydrogenolysis of o-, m- and p-2-anisyl-2β-bornanols over W-5 Raney nickel at atmospheric pressure proceeded to give mixtures of exo- and endo-2-anisyrbornanes. The ortho isomer also gave a substantial amount of the rearrangement product, 1-o-anisylcamphane. Corresponding dehydration products were also found. It is believed that the reaction mechanism is similar to that of acid-catalyzed dehydrations. The adsorption of the hydroxyl group on the nickel catalyst develops a positive charge on the C-2 atom. The intermediate either loses a proton from C-3 to form the bornene or rearranges to give the camphene. Subsequent saturation of the alkenes would yield the observed products.

Hydrogenolysis of the tertiary alcohols over W-5 Raney nickel at high pressures proceeded by a similar mechanism, except that further reduction of the aromatic nucleus took place to form the corresponding cyclohexane derivatives. Under these conditions, the reactions were more stereoselective in giving higher percentages of the less stable exo-anisyl products. This is again explainable on the basis of stronger bonding of the adsorbed intermediates on the catalyst surface.
TRANSIENT INTERMEDIATES IN SbF₅/HSO₃F

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Solutions of antimony pentafluoride in numerous solvents of low nucleophilicity have been reported to easily stabilize high concentrations of alkyl carbonium ions. The ions have been characterized by many techniques, in particular through the use of nmr spectroscopy. It is generally understood that regardless of the carbon skeleton of the cationic source rearrangements generally occur sufficiently fast to preclude the observation of transient intermediates by nmr. Information concerning these transients is therefore slight, although kinetic studies have provided some idea of the nature of specific ionic species and the energetics for several rearrangement paths.

The work discussed in this paper was concerned with gaining further knowledge of the nature of intermediates in the SbF₅-HSO₃F system. Butyl, amyl, hexyl and heptyl halides were reacted with a hydride donor such as methylcyclopentane or methylcyclohexane in 2 molar solutions of SbF₅, mainly at -50°C. Techniques were developed to trap many of the intermediates before equilibrium was attained as well as after. The equilibrated butyl ions gave isobutane and the amyl ions isopentane with little side reaction. Hexyl halides yielded a mixture of the tertiary 2 and 3-methylpentyl and the 2,3-dimethylbutyl cations at -50°C. The relative concentrations of these ions change very slightly up to 65°C. However, above -30°C, 2,2-dimethylbutane was detected and at the higher temperature cracking became severe.

When the alkyl halides are predispersed in the hydride donor it is generally possible to trap intermediates before equilibrium is reached. Thus "kinetically" controlled products may be trapped which differ markedly from the equilibrium distribution. For example, although t-butyl chloride leads to ~100% isobutane, 1 or 2-chlorobutane yield mainly n-butane and isobutyl chloride yields a mixture of ~20% n-butane and 80% isobutane under these conditions.

Similarly, normal amyl cations may be trapped before complete isomerization to the tertiary cation and normal hexyl cations as a mixture of n-hexane, 2-methylpentane and 3-methylpentane with little 2,3-dimethylbutane. Halides which might yield a primary cation are generally but partially converted under these conditions while tertiary halides are completely reacted.
At -50°C a tertiary halide such as 2-chloro-2-methylpentane may be trapped before much rearrangement to the 3-methylpentyl ion. Similarly, 2-chloro-2,3-dimethylbutane and 2-chloro-2,3,3 trimethylbutane may be cleanly converted to the corresponding paraffin.

The experimental observations when taken as a group appear to offer strong support to the suggestion that interconversion of the initial cations in this system occurs considerably through the intervention of protonated cyclopropane derivatives as intermediates. Thus although isobutylchloride yields both isobutane and n-butane, 1-bromo-2-methylbutane and 1-bromo-2-methylpentane yield isopentane and a mixture of 2 and 3 methylpentane with essentially no normal paraffins. These and other results suggest that the formation of n-butane from isobutyl chloride results from the formation of a protonated methyl cyclopropane and its subsequent cleavage to a secondary butyl cation rather then from the direct shift of a methyl group in the isobutyl cation.
Metal Complexes of Phthalocyanine and \( \alpha,\beta,\gamma,\delta \)-Tetraphenylporphyrin as Heterogeneous Catalysts in Oxidative Dehydrogenation

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Polymeric annellated aromatic systems tend to stabilize themselves by taking up hydrogen and may be used as heterogeneous catalysts for oxidative dehydrogenation according to the following scheme:

\[
\begin{align*}
\text{NH} & \quad \text{NH} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[\text{X:cx:x} + \text{RH}_2 \rightarrow \text{X:cx:x} + \text{R} + \text{H}_2\text{O}\]

To extend this kind of reaction into the field of metal-organic polymers, it was tried to synthesize chelate polymers that might have the same quinonic properties as the purely organic system. A good substrate appeared to be: 2,6-dihydroxy-3,7-diketophenazine

This compound gave chelate polymers with many metal ions, some of which were capable of reversible hydrogen transfer as pictured in scheme (1). If, for instance, a mixture of cyclohexadiene-1,4 and air was passed at 150°C over these polymers, benzene and water were formed. Catalytic activity was seen to be dependent on what metal ion was used in forming the chelate polymer. Metal ions that gave an active species were: Fe\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Mn\(^{2+}\), Zr\(^{4+}\), and Ce\(^{3+}\). Inactive were: Mg\(^{2+}\), Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Hg\(^{2+}\), and Cr\(^{3+}\). As the chelate polymers in question are intractable materials that can neither be fused nor dissolved in any solvent, it is very difficult to find the cause of the dependence of catalytic activity on the kind of metal ion in the polymer.

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More tractable metal complexes can be derived from the porphin system that occurs widely in nature and theoretically can be considered capable of reversible hydrogen transfer:

\[
\begin{align*}
\text{18 } \pi\text{-electrons} & \quad \text{16 } \pi\text{-electrons} \\
\text{(2)} & \\
\end{align*}
\]

Contrary to the annellated aromatic systems pictured in scheme (1), the 16-π-electron porphin system cannot be synthesized, which agrees with the fact that the oxidation potential of the 18-π-electron system is much higher than that of most hydroaromatic structures that have been studied.

Therefore it can be understood that the two representatives of this system we studied, phthalocyanine and \( \alpha,\beta,\gamma,\delta \)-tetraphenylporphyrin, were not catalytically active for the oxidative dehydrogenation of cyclohexadiene-1,4. Many of their transition metal complexes were active, however in such a way that a correlation with their electronic structures could be found. If a mixture of cyclohexadiene-1,4 and nitrobenzene was passed over these complexes, benzene, aniline, and water were formed and conversions did not change when the reaction was run for hours at a time. Conversions were surprisingly independent of crystal size and could also be reproduced for different synthetic batches of catalyst. Table 1 gives the results for some bivalent transition metal ions.

### Table 1

Conversions into benzene (% of cyclohexadiene) obtained by passing a nitrobenzene-cyclohexadiene-1,4 mixture over complexes of phthalocyanine\(^a\) and tetraphenylporphyrin\(^b\) with bivalent transition metals\(^c,d,e\)

<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>Metal Ion</th>
<th>Phth.C.</th>
<th>TP.P.</th>
<th>Metal Ion</th>
<th>Phth.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d^5 )</td>
<td>Mn</td>
<td>16</td>
<td>22</td>
<td>Ru</td>
<td>36</td>
</tr>
<tr>
<td>( d^5 )</td>
<td>Fe</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d^7 )</td>
<td>Co</td>
<td>6.2</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d^8 )</td>
<td>Ni</td>
<td>1.4</td>
<td>4</td>
<td>Pd</td>
<td>5</td>
</tr>
<tr>
<td>( d^9 )</td>
<td>Cu</td>
<td>1.5</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d^{10} )</td>
<td>Zn</td>
<td>2.6</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Hourly liquid space velocity (mole cyclohexadiene/mole catalyst/hour) = 1.28.

\(^b\) Hourly liquid space velocity (mole cyclohexadiene/mole catalyst/hour) = 2.13.

\(^c\) \( T = 250^\circ C \).

\(^d\) Mole ratio cyclohexadiene/nitrobenzene = 4.

\(^e\) Conversions into aniline parallel those of benzene.
The $d^5$ and $d^6$ ions show an activity much higher than that of the $d^8$, $d^9$, and $d^{10}$ ions in the same column, which can be understood on the basis of simple crystal field considerations. In the next figure is shown how the $d$-electron energy levels are thought to be split up by the ligands in question:

\[
\begin{align*}
&d_{x^2-y^2} & & d_z^2 & & d_{xz}, d_{yz} & & d_{xy} \\
&\quad & & \quad & & \quad & & \quad \\
&d^8 \text{ (diamagnetic)} & & d^9 & & d^{10} \\
\end{align*}
\]

The $d^8$ (diamagnetic), $d^9$, and $d^{10}$ configurations have a filled $d_{z^2}$ orbital in common. This is an antibonding orbital which is directed perpendicular to the plane of the molecule. If it is filled the molecule is reluctant to take up octahedral substituents, which is illustrated by the fact that there are Fe- and Mn-phthalocyanines known which have taken up two pyridine molecules as extra ligands. Cu- and Ni-phthalocyanine on the other hand are very reluctant to take up extra ligands. Therefore the results in Table 1 do suggest that the catalytic reaction is connected with an attack by one of the reacting species at an octahedral site of the catalyst molecule. A somewhat similar relationship has been found on the decomposition of formic acid\(^3\) and the autoxidation of cumene\(^4\) when phthalocyanine complexes were used as catalysts.

If the numbers in Table 1 are considered in more detail there are several trends which ask for additional explanation. The tetraphenylporphyrin complexes are more active than the phthalocyanines, the second row transition metals seem to be more active than the first row ones, and Zn seems to be somewhat more active than Cu or Ni. Probably here the oxidizability of the complex plays a role and measurements are in progress to study the redox properties of the crystals in question.


A grant to one of us (A.B.I.) from the Monsanto Company is gratefully acknowledged.
Until recently the best known hydroformylation (oxo) catalysts consisted of the simple carbylons of Group VIII transition metals such as Co₂(CO)₈, Ni(CO)₄, etc. However, a new generation of hydroformylation catalysts has been reported in the past few years that consists of substituted metal carbylons having other ligands in addition to carbon monoxide. Some of these ligands impart unusual properties to the catalyst. One particularly interesting catalyst is the triarylphosphine-rhodium(I) complex, RhCl(CO)(P₃)₂. Only fragmentary reports of the use and properties of this complex as a hydroformylation catalyst have appeared. This paper presents the results of a detailed investigation of the rhodium complex RhCl(CO)(P₃)₂ as a hydroformylation catalyst.

Olefins can be catalytically reacted with hydrogen and carbon monoxide using the RhCl(CO)(P₃)₂ complex as a homogeneous liquid phase catalyst to produce aldehyde very selectively (> 99 mol %). Normal reaction conditions of 100-125°C and about 500 psig total reactor pressure are employed.

The significant differences between the present catalyst system, RhCl(CO)(P₃)₂, and others reported in the literature are catalyst stability and the very high selectivity for aldehyde accompanied by a very favorable ratio of linear to branched product. No hydrogenation reactions occur in conjunction with the hydroformylation reaction which result in formation of alcohols and/or paraffin even at high H₂/CO ratios and high hydrogen partial pressure. Also, when employing α-olefin feedstocks isomerization reactions can be effectively controlled to yield aldehydes having a linear content of 75-80% (e.g. normal aldehyde).

The arylphosphinerhodium catalyst system is extremely reactive. Concentrations of rhodium complex in the range of 10⁻³ to 10⁻⁴ M are normally used in homogeneous liquid phase catalytic reaction systems.

Another important feature of the present catalyst system is its unique stability. The rhodium complex catalyst is extremely stable at low partial pressures of carbon monoxide. In catalyst recycle studies the present catalyst and reaction system have been subjected to vacuum distillation at temperature as high as 180°C at 14 mm Hg. No loss in catalytic activity was observed during subsequent reaction cycles when fresh feedstock was added, indicating that no catalyst decomposition occurred. This is in sharp distinction to conventional metal carbonyl hydroformylation catalysts, e.g. Co₂(CO)₈, Ni(CO)₄, and some recently reported substituted metal carbonyl complex catalysts which include alkyl- and arylphosphine, arsine, or stibine ligands.

Although the complex RhCl(CO)(P₃)₂ is normally dissolved in an inert solvent and employed as a homogeneous liquid phase catalyst, as an alternative the rhodium complex may be impregnated upon an inert support such as activated carbon or alumina and used in a conventional fixed bed reactor. Whether employed as a homogeneous liquid phase or fixed bed, vapor phase process, similar mild reaction conditions are used. Comparative results are also given for use of the complex RhCl(CO)(P₃)₂ as both a homogeneous liquid phase and a conventional fixed bed catalyst.
Theoretical work on the diffusion kinetics within supported liquid-phase catalysts (SLPC) has shown that the overall rate of reaction within a porous solid support containing a dispersed homogeneous liquid-phase catalyst depends not only upon the characteristics of the catalyst solution and the reactants, but also upon the relative liquid loading within the support.\(^1\) The results of the theoretical analysis can be summarized as follows,

\[
\text{Conversion} = 1 - \frac{p_0}{p_i} = 1 - \exp \left(-\frac{k_1 k' V_{\text{pore}} E_1 \delta_{\text{liq}}}{F} \right)
\]

\[
E_1 \delta_{\text{liq}} = \delta_{\text{liq}} - \theta + \frac{\tanh \sigma \theta}{\sigma}
\]

\[
\sigma^2 = \frac{k' D_{\text{liq}}}{D_{\text{liq}}}
\]

\[
\theta = f(\delta_{\text{liq}}) = \delta_{\text{liq}} \left( 1 - e^{-\alpha n_{\text{liq}}} + e^{-a} \right)
\]

where \(p_i\) and \(p_o\) are the inlet and outlet partial pressures of the reactant, respectively, \(k_1\) is a gas-liquid partition coefficient, \(D_{\text{liq}}\) is the diffusion coefficient for the reactant in the liquid phase, \(k'\) is a pseudo-first-order rate constant for the conversion of reactant into products in the liquid phase, \(V_{\text{pore}}\) is the total pore volume in the reactor, \(E_1\) is the effectiveness factor for the SLPC, and \(\delta_{\text{liq}}\) and \(\delta_{\text{liq}}\) are theoretical and experimental liquid-loading parameters, respectively. For very active homogeneous liquid-phase catalysts, the theory predicts the existence of an optimum range of liquid loadings outside of which the activity of the SLPC markedly decreases.

The homogeneous hydroformylation of propylene to form n- and iso-butyraldehyde has been successfully used as a model reaction to demonstrate the existence of this optimum. The experiments employed butyl benzyl phthalate solutions of a soluble metal complex dispersed within 3/10 mesh silica gel pellets. A reactant gas mixture composed of 47% hydrogen, 47% carbon monoxide, and 6% propylene was passed over short beds of the SLPC at reaction conditions of 136°C, 490 psig, and two different flow rates. The conversion level, as measured by GLC, for either aldehyde product was at least twice as high at 0.54 liquid loading than at 0.97 liquid loading, despite the fact that there was resistance to diffusion in the gas film external to the SLPC pellets. The percent conversion for the two flow rates is shown in Fig. 1.

Other experimental studies of supported liquid-phase catalysts, including the hydrogenation of propylene and the isomerization of 1-butene, will be briefly discussed.

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Fig. 1. Experimental conversion curves for the hydroformylation of propylene. The points ○ and □ respectively represent gas-phase flow rates of 0.062 and 0.122 cm³/sec at reaction conditions of 136°C and 490 psig.
Use of temperature programmed desorption to study the development of active sites in oxide catalysts

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The temperature programmed desorption technique, developed recently by the authors, has proved useful in the study of the active sites on the surface of some catalysts and of the chemical reactions which occur on these sites. The technique has now been found to be particularly suitable for the study of the growth of active sites in the course of catalyst activation, since the peak areas on the desorption chromatograms provide a measure of the number of active sites and the temperatures at which the peaks are observed are an indication of their strength.

This paper reports the information obtained on the growth and the nature of active sites of alumina and silica-alumina catalysts in the course of catalyst "activation". This information has been complemented by the related information on the catalytic polymerization, hydrogenation and hydrogen exchange of ethylene, chemisorption of hydrogen, the surface area measurements, and X-ray analysis.

For example, when alumina, prepared from aluminum isopropoxide or aluminum nitrate, is evacuated at various temperatures without a pretreatment with air at a high temperature, the weaker sites (the sites responsible for ethylene hydrogenation) gradually increase with the evacuation temperature while the stronger sites (the sites responsible for ethylene polymerization) develop more slowly. However, when the alumina is treated with moist air at 600° and is then evacuated, the number of the stronger sites increases markedly without much change in the number of the weaker sites. The form of alumina (γ) and its surface area remain unchanged during the above treatment with or without air.
A small amount of alkali (Na₂CO₃) added to alumina kills a large part of the weaker sites and all of the stronger ones. Consequently, the activity for ethylene hydrogenation is much reduced and that for ethylene polymerization is completely suppressed. On the other hand, the chemisorption of hydrogen is not decreased as much as is the chemisorption of ethylene.

In contrast to the alumina, silica-alumina catalysts have only one kind of active sites which chemisorb ethylene. Ethylene chemisorption is weaker although the polymerization activity is much higher than on alumina. A comparative study of the silica-alumina catalysts of various compositions will be discussed in connection with the behavior of alumina.
The Exchange of $H_2O^{18}$ with the Oxygen of Promoters on the Surface of Iron Synthetic Ammonia Catalysts.

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Iron synthetic ammonia catalysts are commonly promoted with small amounts of an alkaline or alkaline earth oxide such as $K_2O$, $CaO$ or $MgO$ together with a few percent of an irreducible oxide such as $Al_2O_3$ or $SiO_2$. There has been considerable disagreement on the question of the fraction of the surface covered by these added promoters. Emmett and Brunauer noted that carbon monoxide chemisorption at $-195^\circ$ covers only about 40% of the surface of a catalyst containing a few percent postassium oxide and aluminum oxide as promoter. They concluded that about 60% of the surface was covered by promoter. Scholten and coworkers measured the exchange between the deuterium of heavy water and the hydrogen of the OH groups believed present on the promoter molecules on the iron surface. They concluded that probably about 30% of the surface was covered with promoter. It has also been suggested that the promoter concentration on the surface may be exactly the same as in the interior of the catalyst crystals and that the smaller percentage coverage of the surface of the promoted catalyst with CO chemisorption may be attributed to the influence of the promoter molecules on the electronic and hence chemisorptive characteristics of the surrounding iron atoms. To answer this question from another approach the present work was carried out: $H_2O^{18}$-$H_2$ mixtures were permitted to equilibrate with pure iron and promoted iron catalysts. The gas phase was then analyzed for the ratio $H_2O^{18}/H_2O^{16}$ and calculations made as to the amount of the $K_2O-Al_2O_3$ promoter on the catalyst surface. On the same catalysts used for the exchange experiments, the chemisorption of carbon monoxide at $-195^\circ$ was also measured.
The results may be briefly summarized, as follows:

1. On an iron catalyst containing 1.06% K$_2$O and .52% Al$_2$O$_3$, the oxygen content corresponded to about 58% surface coverage with promoter molecules. This was in excellent agreement with the carbon monoxide chemisorption measurements which indicate 41 to 44% of the surface was iron.

2. On pure iron catalyst 927 to which no promoter had been purposely added, three runs showed 7, 8 and 18% coverage with promoter. This is probably due to the small amount of Al$_2$O$_3$ known from other work to usually be present in these "pure iron catalysts". As much as 0.15% Al$_2$O$_3$ may have been present and could reasonably have yielded the surface promoter content indicated. The CO chemisorption showed a coverage of 86% of the surface with iron on the sample on which the exchange showed 18% coverage with promoter.

3. A sample of pure iron catalyst prepared by precipitation and reduction showed a surface oxygen content equivalent to coverage of only 1% of the surface. On this same sample the CO chemisorption volume was 1.13 times the volume of nitrogen required to form a monolayer. This is about the value to be expected for chemisorbed CO over the entire surface of the iron.

4. In the course of this work it was also established that three or four hours evacuation of a sample of iron catalyst containing chemisorbed and physically adsorbed carbon monoxide was sufficient to remove all the physical adsorption without removing chemisorption. The latter came off at the rate of about 7% per hour at -78°C. This is in agreement with previous observations.

In summary, the H$_2$O$^{18}$ exchange work reported here clearly shows that the K$_2$O-Al$_2$O$_3$ promoter content of a standard doubly promoted iron synthetic ammonia catalyst covers about 60% of the surface of the iron leaving only 40% of the surface as metallic iron. This result agrees well with conclusions previously drawn from low temperature CO chemisorption work.
New information about the structure of Cu\(^{+2}\) in \(\gamma\)-alumina composites has been obtained by X-ray K-absorption edge spectroscopy. Previously we have measured Cu\(^{+2}\) supported on \(\gamma\)-alumina by X-ray diffraction (XRD) and by electron paramagnetic resonance (EPR). The XRD studies of samples calcined at 500\(^\circ\)C were able to detect copper oxide (CuO) crystallites on relatively low surface area alumina (72 m\(^2\)/g) at a copper concentration of about 10\% by weight. After heating such samples to 700\(^\circ\)C, one was able to detect copper aluminate (CuAl\(_2\)O\(_4\)) crystallites. The EPR study dealt with high surface \(\gamma\)-alumina (301 m\(^2\)/g) with copper impregnation of 5-10\% by weight. The EPR signals were assigned to atomically dispersed Cu\(^{+2}\) species and were fitted to a tetragonally distorted octahedral spin Hamiltonian of a 3d\(^8\) system. XRD measurements on these samples failed to detect any copper-containing phase. The present investigation provides information about the molecular structure of the Cu\(^{+2}\) surface phases that supports previous work, and also supplements it.

The X-ray K-absorption measurements were made on a General Electric XRD-5 spectrometer. The radiation source was a chromium CA7-XRAY diffraction tube. A LiF crystal was used to obtain a monochromatic beam and the sample was introduced at the position of the filter in regular diffraction measurements. Three slow scans of 0.072\(^\circ\)/hr gave reproducibility within ± 0.002\(^\circ\).

The results showed that pure CuAl\(_2\)O\(_4\) has an absorption edge of 0.020\(^\circ\) lower than that of bulk CuO, which corresponds to an energy of 7.0 ± 0.7 ev higher for the aluminate. The supported copper was detected by the absorption edge technique in all samples and showed that on the high surface alumina the copper is in a CuAl\(_2\)O\(_4\) "surface phase" even at the high concentration (~ 10\%) and at a low calcination temperature (300\(^\circ\)C). The low surface alumina with 10\% by weight copper on it calcined at 500\(^\circ\)C showed mainly a CuO "surface phase"; the shift towards the CuAl\(_2\)O\(_4\) value was of 1.4 ± 0.7 ev only. However, after calcining the same sample at 900\(^\circ\)C the absorption edge showed unequivocally a CuAl\(_2\)O\(_4\) "surface phase."

These results demonstrate in general the power of the X-ray K-absorption edge spectroscopy to obtain information of the molecular structure of supported catalysts, and in particular show that many so-called copper oxide on alumina catalysts actually consist of copper aluminate on alumina. The stability of the aluminate compound is readily understood if one bears in mind that the alumina and the aluminate both have a spinel type structure, namely that the bond distances are determined by the close packing of octahedral arrangement of six oxygens. CuO crystallites would form only on relatively low area surfaces at high concentrations and even then there is strong tendency at higher temperatures for them to penetrate into the alumina lattice.
ABSTRACT

The First North American Meeting of the Catalysis Society

ADSORPTION STUDIES USING MOSSBAUER SPECTROSCOPY.
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Catalyst samples containing 1-2% iron supported on silica gel and eta-alumina were prepared by impregnation with Fe-57 enriched nitrate solutions. In the ferric oxide state, no x-ray diffraction pattern for an iron compound was observed, and an unusually large quadrupole splitting was found in the Mossbauer spectra indicating that the iron existed in a highly dispersed state with estimated average crystallite diameters of less than 50 angstroms.

The Mossbauer spectrum of the oxidized and outgassed silica gel sample was a doublet with a quadrupole splitting of 1.72 mm/sec and a chemical shift of +0.56 mm/sec relative to a standard sodium nitroprusside crystal. On adsorption of ammonia the quadrupole splitting decreased to 1.24 mm/sec, but the chemical shift remained unchanged. The quadrupole splitting gradually increased with temperature on outgassing and approached the initial value at 300°C. These results show that the electric field gradient at the iron site decreases on chemisorption of ammonia, but very little change takes place in the electron density of the 3d and 4s orbitals of the ferric ion.

The Mossbauer spectrum of this sample reduced in flowing hydrogen at temperatures as high as 600°C was a triplet that appeared to be the sum of the superposition of two doublets. One doublet was assigned to the ferrous valence state with a quadrupole splitting of 1.55 mm/sec and a chemical shift of +1.30 mm/sec. The other was assigned to a ferric state with a quadrupole splitting of about 1.00 mm/sec and a chemical shift of +0.98 mm/sec. No evidence was obtained to indicate that any of the iron had been reduced to the zero valence state. The adsorption of ammonia and trimethyl ammine on this sample caused the doublet assigned to the ferric state to almost vanish while the quadrupole splitting of the ferrous doublet increased to 1.70 mm/sec and the chemical shift remained unchanged. Apparently, the surface complex that is being observed in this case does not require a dissociative adsorption mechanism since identical results were obtained for both ammonia and trimethyl ammine. Again the original spectrum could be reproduced on outgassing at elevated temperatures. The adsorption of butene-I and CO produced similar but much smaller changes in the Mossbauer spectra. The same type of study was carried out on the alumina supported sample. The results are discussed in terms of the formation of surface complexes.
Adsorption of Oxygen and Hydrogen on Platinum
Part I. Unsupported Metal

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ABSTRACT

Before the adsorption of hydrogen and oxygen, separately or in succession, can be used with confidence to determine the surface area of supported platinum catalysts, it is important to verify for the unsupported metal the stoichiometry of the following reactions, where Pt denotes a surface metal atom:

\[ \text{Pt} + \frac{x}{2} \text{O}_2 \rightarrow \text{Pt} \text{O}_x \quad (1) \]
\[ \text{Pt} + \frac{y}{2} \text{H}_2 \rightarrow \text{Pt} \text{H}_y \quad (2) \]
\[ \text{PtO}_x + (x + \frac{z}{2}) \text{H}_2 \rightarrow \text{PtH}_2 + x\text{H}_2\text{O} \quad (3) \]

We have determined the values of \( x \), \( y \) and \( z \) on platinum black at room temperature and a gas pressure of 50 torr. By introduction of the gases at low temperatures prior to equilibration at room temperature, sintering of the samples could be avoided, as shown by periodic checks of their BET nitrogen surface area. From the BET data the number of surface platinum atoms was calculated by means of the averaged surface density of \( 1.19 \times 10^{15} \) sites cm\(^{-2}\).

Following reduction of the samples in hydrogen, the residual hydrogen that could not be pumped off at 120°C was determined by exchange with deuterium. All adsorption measurements were corrected for this residual hydrogen.

The work was carried out in two separate adsorption systems by both gravimetric and volumetric techniques. Results were obtained that could not be obtained by either technique separately. Thus, the gravimetric results showed directly that water formed in the titration does indeed spontaneously leave the surface of platinum black at room temperature, as
suggested by equation (3). Volumetric results provided the complementary information that, as water leaves the surface after a titration, no further hydrogen is taken up by the metal.

The average values of $x$, $y$ and $z$ for the volumetric work are summarized below:

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.84</td>
<td>0.86</td>
<td>0.85</td>
</tr>
</tbody>
</table>

These results are in agreement with those of many other investigators. In particular, they show that at room temperature and 50 torr pressure, the amounts of hydrogen and oxygen taken up by platinum black surfaces are about equal and almost equal to, but less than, a monolayer. Furthermore, since $y$ is almost equal to $z$, the titration equation (3) can be written, as an excellent first approximation, as:

$$\text{PtO} + \frac{3}{2} \text{H}_2 \rightarrow \text{PtH} + \text{H}_2\text{O}.$$  \hspace{1cm} (4)

Thus the stoichiometry of equation (4) proposed by several workers appears vindicated, at least on unsupported platinum.
The Adsorption of Nitric Oxide on Chromia-Alumina

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It was observed during the studies of the catalytic reduction of NO by CO
that oxygen is a strong poison for this reaction on supported chromium catalysts. It
was therefore of interest to follow the NO adsorption on reduced and oxidized
surfaces of supported chromia. Chromia is well suited for such a study because
under proper experimental conditions the oxidation-reduction treatment can be
confined to the surface.

The NO adsorption was followed by a continuously recording Cahn electro-
balance. Shrinkage of the sample in the course of the study and adsorption on the
support were allowed for. Adsorption isotherms were taken at -78, 0, 90 and 150°C
and rate measurements at 0, 45, 90, 120 and 150°C. A higher temperature range
was excluded to avoid the decomposition of NO.

The isotherms in the pressure range from 0.1 to 300 Torr NO are best
described by a linear relationship between the logarithmic coordinates of
pressure and amount adsorbed, i.e. they are of the Freundlich type. On the
reduced surface the isotherms intersect at a common point which corresponds to a
monolayer coverage. This coverage is equivalent to roughly one NO molecule per
chromium site in the surface. It opens up a possibility for assessing the chromia
surface of a supported catalyst by NO adsorption at or near ambient temperatures. There is no similar behavior in the case of the oxidized surface, for which the
isotherms are nearly parallel which indicates that the "monolayer coverage" on
this surface changes with temperature.

The adsorption on both surfaces is unmistakably a chemisorption process
being slow, specific with respect to the chromium atoms in the surface, and taking
place at temperatures far above the critical temperature. However, the observed
isosteric heats of chemisorption which could be measured only at medium coverages
of 0.3 - 0.4 were surprisingly low, of the order of 5 kcal/mole on both surfaces. This notwithstanding, considerable desorption hysteresis was observed. From the
oxidized surface the adsorbed NO could be removed by pumping at 200°C as evidenced
by the return to the original weight. From the reduced surface at least 90% of
the NO could be reversibly disengaged at 250°C, while the remaining amount was
decomposed by the surface and the oxygen used up for the oxidation of the surface.

The kinetics of the chemisorption on the oxidized surface are well described
by a continuous Elovich plot. On the reduced surface a sharp discontinuity in
the Elovich plots is observed at all temperatures at a coverage corresponding to
about 0.25 of a monolayer. The chemisorption rates at coverages corresponding to
0.1 of the monolayer coverage are faster on the reduced surface by 2 - 3 orders of
magnitude than on the oxidized surface. The temperature coefficients of the
chemisorption process as assessed from the change of the slope α of the Elovich
plots with temperature are negative for both surfaces being -1.4 and -0.3
kcal/mole for the oxidized and reduced surfaces, respectively. Such an unusual
behavior of the NO chemisorption has been observed by other investigators on
widely different surfaces.

The relevance of the chemisorption rates on both surfaces and of their
negative temperature coefficients to catalytic processes in which NO participates
is discussed. A tentative model is advanced to explain the sharp break in the
Elovich plot for the reduced surface.
A fundamental understanding of catalysis requires a knowledge of the
detailed nature of surface species. While no complete catalytic reactions
are dealt with here, the structures of a number of surface species formed
on vanadium are examined by infrared spectroscopy. The metal adsorbent
consists of finely divided metal particles dispersed in a hydrocarbon
oil matrix. The experimental technique involves evaporating vanadium
from a heated tungsten filament in an infrared cell. Since the metal
particles are in an oil matrix the adsorbate molecules must compete with
the saturated hydrocarbon molecules of the matrix for adsorption sites.
Our results indicate that the oil matrix does not dominate the adsorption
sites.

Typical of the alcohols adsorbed, n-propanol produced bands at 1150,
1105, 1075, 1020, 980, 888, 590 and 465 cm\(^{-1}\). Comparison of these bands
to those of liquid n-propanol at 1140, 1100, 1075, 1060, 1020, 990, 972
(weak), 918 (weak), 908 (weak), 890, 860 (weak) and 460 cm\(^{-1}\) suggests
strongly that a surface alkoxide structure is formed by adsorbed n-
propanol. The adsorbed species bands are all assigned to the same CH\(_3\)
rocking and skeletal stretching vibrational modes as occur in liquid n-
propanol except for the strong band at 590 cm\(^{-1}\) which has no counterpart
in liquid n-propanol. This band is tentatively assigned as primarily
involving metal-oxygen stretching. Other alcohols studied include methanol, ethanol, allyl-alcohol, 2-propanol, 2-butanol, isobutanol, and t-butanol. In general alkoxide surface structures were produced. The order of reactivity followed the trend; primary > secondary > tertiary.

Acetaldehyde produced bands for the adsorbed species at 1740, 1660, 1575, 1240, 1150, 1095, 1065, 960, 930, 890 and 580 cm\(^{-1}\). The most intense bands are those at 1150, 1095 and 1065 cm\(^{-1}\). Comparison of these to liquid ethanol bands and the bands produced by adsorbed ethanol on V lead to the conclusion that an alkoxide structure predominates on the surface. The 580 cm\(^{-1}\) band is tentatively assigned as primarily involving metal-oxygen stretching for this species. The weak band at 1740 is taken as indicating a small amount of acyl structure on the surface. The very weak band at 1575 is probably indicative of a little bit of unsaturated species.

Propionaldehyde gave similar results except for the existence of much more unsaturated material as indicated by a medium intensity band at 1545 cm\(^{-1}\).

Ethylene oxide and propylene oxide gave infrared bands for surface alkoxide structures and gas phase alkenes.

Acetone and methyl ethyl ketone produced alkoxide structures but in lesser quantities than previous compounds. Methyl ethyl ketone also produced a small amount of an unsaturated species.

Diethyl ether and tetrahydrofuran gave no infrared evidence of adsorption. This is interpreted as indicating that a purely coordinate bond of a lone pair of electrons on oxygen to vanadium is not a stable
structure. Methyl vinyl ether decomposed on the surface to give a methoxide surface species.

Adsorption of CO₂ produces a very weak band at 1900 cm⁻¹ which we ascribe to chemisorbed CO produced by decomposition of CO₂ and a medium intensity band at 1560 cm⁻¹ which together with a weak band at 1340 cm⁻¹ is indicative of a structure like a free organic acid.

Oxygen adsorption produces a broad adsorption in the 900-500 cm⁻¹ region which is characteristic of vanadium oxides and a band at 1015 cm⁻¹ which is characteristic of vanadium-oxygen double bond.

In summary for vanadium it appears that the surface chemistry, where alkoxides have been found to predominate, is quite similar to its general inorganic chemistry where alkoxides are also numerous and stable.
PERTURBATION OF SURFACE HYDROXYL GROUPS ON POROUS VYCOR GLASS BY AROMATIC $\pi$-ELECTRON SYSTEMS

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ABSTRACT

The reaction of benzene and several other monosubstituted benzenes with porous Vycor glass surfaces has been studied in detail by means of infrared absorption spectroscopy. Complementary thermodynamic data were calculated from adsorption isotherms obtained using a sensitive microbalance. The credibility of a charge-transfer mechanism is discussed.

The reaction of benzene with hydroxylated porous Vycor glass surfaces at room temperature takes place reversibly, and mainly between benzene molecules and free surface hydroxyl groups on both silicon and boron atoms. This process results in a progressive weakening of surface O-H bonds, which effect is manifested by a shift in the free hydroxyl stretching frequency $\Delta v_{OH}$, as observed in the infrared absorption spectrum of the glass surface.

Benzene adsorption on porous Vycor glass is not entirely similar to that on non-porous silicas. For the former, porosity effects are consistently found which suggest enhanced interactions between benzene molecules and surface hydroxyl groups within the micropore structure. Such cooperative effects, as indicated by radical changes in various spectroscopic parameters, are a complex function of many variables, and probably involve extensive molecular rearrangement on the glass surface.

Surface BOH groups appear to be more reactive than SiOH groups with respect to benzene adsorption. Because boron is more electronegative than silicon, this order of reactivity is in accord with the charge-transfer interaction mechanism subsequently deduced for the benzene-porous Vycor system. In support of this mechanism, the infrared results indicate that interaction between surface free hydroxyl groups and benzene molecules is established via the $\pi$-electrons of the aromatic nucleus and with the hydroxyl proton.

Thermodynamic data show that benzene adsorption on porous Vycor glass is exothermic and gives rise to major adsorption hysteresis at high surface coverages. The adsorption isotherms exhibit Brunauer Type V behavior up to the monolayer point, the amount of benzene adsorbed being a linear function of the relative pressure in this region. At a given equilibrium pressure, more benzene is adsorbed on a 500° degassed surface than for one degassed at 750°, again indicating the importance of the free hydroxyl group as an adsorption site; i.e., the greater concentration of free hydroxyl groups on the 500° degassed surface gives rise to higher adsorption.
Analysis of the pore structure in terms of the Barrer-de Boer theory suggests that the pore geometry is one of cylindrical symmetry which in turn contain slightly enlarged spherical cavities.

The differential enthalpy and entropy of adsorption, as calculated directly from the isotherms, both show maxima at a surface coverage of \( \theta = 0.75 \). These maxima occur in the same range of surface coverages for which radical changes were found for the various spectroscopic parameters. This fact supports the idea of increased interactions within the glass pore system. No such effects were found for non-porous silica.

The entropy of adsorption for two extreme models, complete immobility and mobility, was calculated for the benzene-porous Vycor system as a function of surface coverage. At a coverage of 0.5 the best model is that for complete species mobility, while at lower coverages (\( \theta \leq 0.1 \)) the benzene molecules appear to be quite immobile. The validity or appropriateness of either model was based on theoretical statistical mechanical calculations for the expected entropy change. Thus at a coverage of 0.5 the adsorbed molecules were best described as having one degree of rotational freedom perpendicular to the aromatic nucleus and the glass surface. The benzene molecules also have significant translational freedom in the two-dimensional plane. Apparently, at low coverages, the first small amount of benzene adsorbed interacts strongly, and is followed by a gradual change-over to mobile adsorption at higher coverages. At a coverage of about 0.6, filling of the micropore structure is initiated, and is accompanied by maxima in the enthalpy and entropy of adsorption.

The residence time for a benzene molecule on a porous glass adsorption site may vary by as much as 10 orders of magnitude, indicating a high degree of surface heterogeneity.

An analysis of the mode of surface interaction for benzene and several other monosubstituted benzenes with the surface of porous Vycor glass in terms of the Mulliken-Puranik theory strongly suggests a charge-transfer process. This theory developed by Puranik(1) for homogeneous systems uses Mulliken's charge-transfer theory(2) to give the functional dependence of the relative free hydroxyl shift \( \Delta \nu_{\text{OH}}/\nu \) and enhanced bond intensity \( A \) on the donor ionization potential \( I_D \), acceptor electron affinity \( E_A \), coulombic interactions \( W \), bond polarity \( \lambda \) and orbital overlap \( S \), i.e.,

\[
\Delta \nu_{\text{OH}}/\nu = \frac{(5\lambda C^2 S^2)}{2(I_D-E_A-W)^2} \quad (a)
\]

\[
\Delta \nu_{\text{OH}}/\nu = \left[ 5\lambda S \frac{(\partial S^2/\partial r)}{2} \right]/2 \lambda_p \left( \frac{\partial^2 E}{\partial r^2} \right) \quad (b)
\]

The oxy- and nitro-substituted aromatics studied interact mainly through their hetero atoms and not through the \( \pi \)-electron system. Anisole may be an exception and show two simultaneous points of attachment; i.e., through the \( \pi \)-electron system and also through the substituted oxygen atom. For

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fluoro- and methyl-substituted benzenes it is believed that the surface bond is established via the aromatic \( \pi \)-electron system and with an antibonding orbital from the surface hydroxyl group -- most probably from the surface hydroxyl group. Thus one observes a net decrease in bond order for the free hydroxyl group, as verified by the infrared results. The antibonding orbital of the proton is believed to interact with the aromatic \( \pi \)-system along one of the carbon-carbon lengths, forming an asymmetrically bonded complex.

For the three groups of adsorbates studied, the following increasing order of reactivities was found:

\[
\phi-\text{NH}_2 \gg \phi-\text{OCH}_3 > \phi-\text{OH} > \phi-\text{OCH}
\]

\[
\phi-\text{F} > \phi-\text{CF}_3 > \text{C}_6\text{H}_{12}
\]

\[
\text{sym}-\phi-[\text{CH}_3]_3 > \text{p}-\phi-[\text{CH}_3]_2 > \phi-[\text{CH}_3] > \phi-\text{H}
\]

These orders are explainable by orbital overlap and induction considerations.

A crude anharmonic oscillator treatment of the surface hydroxyls on porous Vycor glass leads to the fact that the energy of interaction \( D_{\text{OH}} \) is directly proportional to the free hydroxyl shift \( \Delta \nu_{\text{OH}} \); i.e.,

\[
D_{\text{OH}} = 0.032 \Delta \nu_{\text{OH}} \text{ kcal/cm}^{-1}
\]
The Pore Geometry of Raney Nickel

By

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The pore geometry of Raney nickel has been calculated from nitrogen isotherms at -195°C. The properties of this catalyst are known to vary with the composition of the starting nickel-aluminum alloy \(^1, 2\) and with the conditions under which alloy is allowed to react with alkali \(^3, 4\). The Raney nickels studied were therefore prepared by a variety of procedures and from three alloys containing different amounts of the intermetallic compounds NiAl\(_3\) and Ni\(_2\)Al\(_3\), the precursors of the nickel catalyst.

For a single activation procedure, the starting alloy had no significant effect on the pore structure of the final catalyst. It is concluded that Raney nickels originating from NiAl\(_3\) and from Ni\(_2\)Al\(_3\) have similar porosity.

Metallographic studies of the reaction of alloy with aqueous sodium hydroxide indicated that NiAl\(_3\) underwent markedly preferential reaction to Ni\(_2\)Al\(_3\) but that in either alloy phase, an advancing interface type of reaction occurred, the solid to one side of the interface being Raney nickel, to the other, unreacted alloy. Isotherms from partially extracted catalyst were consistent with this interpretation. Both surface area and pore volume appeared to be generated directly during the oxidation.
and dissolution of aluminum, the formation of the final pore structure involving no major changes of the material produced initially.

The only marked variation in pore structure observed was between catalysts prepared at moderate temperature ($50^\circ C$) and those prepared in boiling aqueous sodium hydroxide ($107^\circ C$). Typical data for such catalysts, which will be called the low (L.P.V.) and high (H.P.V.) pore volume types, respectively, may be summarised in terms of surface area, pore volume and mean pore diameter as calculated for open ended pores of cylindrical cross-section.

<table>
<thead>
<tr>
<th>TYPE</th>
<th>EXTRACTION TEMP. ($^\circ C$)</th>
<th>B.E.T. AREA ($m^2/g$)</th>
<th>PORE VOLUME (cc./g)</th>
<th>MEAN PORE DIAMETER (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.P.V.</td>
<td>50</td>
<td>100</td>
<td>0.064</td>
<td>26</td>
</tr>
<tr>
<td>H.P.V.</td>
<td>107</td>
<td>82</td>
<td>0.125</td>
<td>61</td>
</tr>
</tbody>
</table>

It was also found that if catalyst extracted at $50^\circ C$ were further treated in aqueous sodium hydroxide an increase in pore volume and decrease in surface area, i.e., change from the L.P.V. to H.P.V. type, resulted. Treatment with boiling water, however, decreased area but did not alter pore volume appreciably. These results suggest that the transformation from the L.P.V. to the H.P.V. type involves the removal of residual alumina from pores and sintering of the nickel. Other data indicate that residual alumina has a relatively low surface area.

Acknowledgement: The authors gratefully acknowledge the financial support of this work by the W.R. Grace Company.
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DISPROPORTIONATION OF CARBON MONOXIDE OVER IRON AND SILICON-IRON SINGLE CRYSTALS


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The disproportionation of carbon monoxide over metallic iron has been studied by numerous workers. However, the conclusions reached regarding the precise sequence of steps involved in the catalyzed reaction are found to be at variance. For instance, iron, cementite, Hägg carbide, a carbonyl and a magnetite-iron interface have all been suggested as the active catalytic species. The intimate details of the disproportionation are further clouded by an incomplete understanding of the very important role played by hydrogen. To date it appears that the latter can modify the catalytic mode both directly, by promoting the rupture of the carbon-oxygen bond and indirectly, by regenerating a completely carbided catalyst which is now regarded as being inactive. Furthermore, water vapor can be substituted for hydrogen to produce the same effect. It is also rather puzzling that the reaction rate should reach a maximum between 500-600°C, although it has been stated that there is a resurgence in activity above 800°C.

The present study was originally undertaken as an attempt to differentiate between the above possibilities by employing high purity single crystals, having specific orientations, of both iron and 3.25% silicon-iron. The reasons for studying both iron and silicon-iron are three fold: (1) The α → γ transformation, which occurs at 723°C for the iron-cementite system and at 738°C for the iron-graphite system, can be completely suppressed by the addition of 3.25% silicon. The reactivity associated with the B.C.C. ferrite and F.C.C. austenite lattices can then be compared. This is desirable since it is possible that the increase in reaction rate observed above 800°C is due either to the greater solubility of carbon in the B.C.C. lattice or to a modified chemisorption step. (2) Although it is relatively easy to carbide iron powder above 200°C, 3.25% silicon-iron is carbided only slightly at 830°C in hydrogen-heptane mixtures. This is clearly an advantage in determining the role of iron carbides during the reaction. (3) In contrast to iron crystals, it is not too difficult to arrange for arrays of pure edge and pure screw dislocations to intersect different faces of the same single crystal of silicon-iron. By suitable heat treatment, the edge dislocations are then polygonized, forming linear arrays which are sessile under the conditions utilized for disproportionation. It is important to know whether such dislocations act as active sites for nucleation at the surface or whether perhaps they catalyze a solid-state reaction between carbon and iron. That the dislocations in both iron and silicon-iron are preferentially decorated by carbon atoms is now well known.

The nature and formation of the solid products of the reaction have been studied by optical microscopy, transmission and reflection electron diffraction, scanning electron microscopy, x-ray diffraction and microgravimetric analysis.
Both iron and silicon-iron single crystals were poor catalysts for the disproportionation of pure carbon monoxide. When a mixture of 90.6% CO-9.4% H$_2$ was employed, an induction period occurred prior to the growth of carbon. During this time an oxide formed at the crystal surface. Reflection electron diffraction showed this oxide to be composed of single crystal maghemite which had grown epitactically (or possibly topotactically). In the case of iron, the maghemite took the form of needle-like plates; on the silicon-iron, it grew as a complete film. It was found that the oxide film formed faster on the silicon-iron than on the iron when identical experimental conditions were employed. Significantly, the rate of oxidation depends on the water vapor pressure. In all experiments the reaction temperature was 550°C.

In the case of iron crystals the oxide is superceded by a carbon film and in turn by the appearance of a carbide. At a later stage, whisker growth also becomes prominent in the product layer. It is also noteworthy that mechanical and electropolishing of the iron crystal, after removal of the product layer, revealed small needle-like nuclei which are probably carbidic in nature. Significantly neither carbide nor whisker growth was observed in the carbon film formed on the silicon-iron crystals or in the crystals themselves. The induction period for carbon growth on silicon-iron is about half that noted for pure iron and must be linked with the faster oxide growth. Further, for both iron and silicon-iron, the rate of oxide formation and the length of the induction period are dependent on the water vapor pressure.

Quite apart from substantiating any previous theory we now propose a new mechanism for the disproportionation of carbon monoxide over iron in which the oxide maghemite plays a vital role. During the growth of maghemite in the presence of even trace quantities of water vapor, cationic vacancies can be readily formed due to the displacement of iron ions by hydrogen ions. It is suggested that this extremely reactive hydrogen species is of considerable importance in the catalytic breakdown of carbon monoxide.
Production, Properties and Reaction of Metallic Sodium Films in Porous Vycor Glass

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As part of a program of studying the elementary processes taking part in heterogeneous catalysis, we have studied the preparation, properties and reactions of a sodium film produced in pores of Vycor glass (Corning No.7930). The purity of this silica material, its high surface area and uniform porosity of 40 Å make this material highly suitable for carrying out reactions, since the pores are so small that light can be transmitted through the body of the support and used to carry out photochemical reactions within the pores. This property has been utilized effectively by Turkevich and Fujita in the preparation and stabilization at room temperature of methyl radicals. The purpose of this investigation was to prepare a film of sodium of at most three monolayer thick in order to carry out reactions within the pores of the Vycor glass—decreasing thereby the diffusion rate of the primary reaction product and thus facilitating the study of active species on surface. It was hoped that methyl radicals could be prepared by direct reaction of sodium with methyl iodide rather than photolysis. It turned out that this reaction does not take place at room temperature and this led to the investigation of the basic problem: under what conditions free electrons from metal such as sodium transfer to an adsorbed reactive species such as methyl iodide.

A number of subsidiary problems was investigated in the course of this work: the behavior of sodium in ammonia solutions in small pore, the electron spin properties of sodium films and finally various types of photocatalytic reactions of methyl iodide. The sodium was deposited from sodium in ammonia solution. The ESR characteristics of this solution were investigated both in bulk and when the solution is absorbed in the 40 Å pores of the Vycor glass. The change in the ESR signal on evaporation of the sodium allowed us to study the transitions of the electron from an ammonia cage to a cluster of sodium atoms and finally to the sodium film on the surface of the silica. The behavior of sodium in deuterio ammonia was also studied. The evaporation was carried out in a vacuum quartz glass system with "break off" connections. The purity of the
system was such that the conductor electrons in sodium could be estimated by their ESR signal at room temperature. The film was stable to about 400°C when it reacted with the silica. Transfer of electrons took place readily with oxygen, chlorine, anthracene, and metal-free phthalocyanine. There was no reaction with hydrogen up to 400°C.

There was no electron transfer with methyl iodide at liquid nitrogen temperature. On heating to 40°C for a minute a fast reaction took place with the disappearance of the sodium electron signal and no appearance of the methyl radical signal. Irradiation at liquid nitrogen temperature with near U.V. light from mercury arc produced a very large signal of the methyl radical when sodium was present on the walls of the glass. Irradiation with visible light absorbed by phthalocyanine-sodium complex also produced dissociation of the methyl iodide into methyl radicals.

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Selectivity and Stoichiometry of Copper Oxide in Propylene Oxidation

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Abstract

In the oxidation of propylene over copper oxide the relationship between selectivity of the catalyst and identity of its solid-state surface properties has not been established although several investigators have reported that the selective oxidation to acrolein is sensitive to temperature and propylene-to-oxygen ratio. In our experiments we selected the surface of a cuprous oxide crystal for the kinetic measurements of the formation of acrolein and carbon dioxide at 350°C. The cuprous oxide was prepared inside the quartz reactor subsequently used for catalytic studies. The crystal was grown by oxidizing a thin copper foil (0.001 to 0.003 inches) in air at 1030°C, and then annealing it at 1115°C. The catalytic studies were carried out at 350°C, with helium as the carrier gas. In addition to the chemical determinations of the product distribution (by GC) a series of simultaneous in-situ measurements were made of the electrical conductivity and optical properties (reflectance spectra) of the single-crystal catalyst.

Under our experimental conditions it was observed that changes in the composition of the feed gas caused marked changes in electrical conductance of the catalyst. The addition of propylene to the oxygen-containing feed stream diminished the conductance of the crystal. But for a fixed partial pressure of olefin, the addition of oxygen resulted in a corresponding increase in electrical conductance. Also the reflectance measurements demonstrated two distinct spectra with variation in the olefin-oxygen ratio.

With reference to the known electrical and optical characteristics of the cuprous-oxide single crystal it was established that during catalytic reaction the cuprous-oxide phase may be stabilized even at relatively high partial pressures of oxygen admixed to propylene. Comparison of the kinetic data with the physical measurements demonstrated that catalyst selectivity is very sensitive to the stoichiometry of the surface phase of the catalyst. The most active solid phase for acrolein formation was found to be stoichiometric or copper-rich cuprous oxide. On the other hand, oxygen-rich cuprous oxide and cupric oxide favor complete oxidation of propylene to carbon dioxide. The rates of formation of acrolein and carbon dioxide appear to be a function of the oxygen partial pressure, but relatively independent of the propylene partial pressure.
The results are interpreted in terms of a model involving surface-sorbed oxygen and electronic charge carriers. Specifically, the surface density of several oxygen species depends not only on the partial pressure of gaseous oxygen and propylene but also on the defect structure of the catalyst. The distribution of surface-active species is inferred from a theoretical analysis of the degree of occupancy of surface-state energy levels associated with the cuprous oxide surface. Such a model also offers an interesting interpretation of the role of promoters in propylene oxidation over copper-oxide catalyst.
The ortho-para $\text{H}_2$ conversion may proceed by either a dissociative or a non-dissociative mechanism. If the process is dissociative, the $\text{H}_2$-$\text{D}_2$ exchange should proceed at a comparable rate and with the same kinetic behavior in the absence of a large isotope effect. If the process is non-dissociative, then the reaction may be presumed to be a paramagnetic conversion, and the $\text{H}_2$-$\text{D}_2$ exchange cannot occur. It has always been supposed that the paramagnetic conversion must reflect unpaired electrons on the catalyst surface. The reason for this is that the transition probability is dependent upon the square of the magnetic moment of the paramagnetic center. Since nuclear magnetic moments are about three orders of magnitude lower than that for an unpaired electron, calculations suggest that reasonable transition probabilities could not be obtained through interaction of $\text{H}_2$ with nuclear moments. It is the purpose of this paper to point out that this supposition may be untrue.
The kinetics of the H$_2$-D$_2$ exchange, the o-p H$_2$ and p-o D$_2$ conversions were studied on the surface of a very pure alumina, with and without a portion of the sites selectively poisoned with CO$_2$. These data were supplemented with results obtained from surfaces dehydroxylated to different extents. When the alumina was dehydroxylated below 525°C, at 0°C the rate of the ortho-para H$_2$ conversion, R$_H$, was only a little higher than the rate of the H$_2$-D$_2$ exchange. Both rates fell in a parallel manner as the surface was poisoned with CO$_2$ in a way which eliminated the strongest sites first. Both rates fell to less than 1% of their initial values at about 16 $\times$ 10$^{12}$ CO$_2$/cm$^2$. At -195°C, the exchange reaction was too slow to measure, but both conversion reactions (H$_2$ and D$_2$) had comparable and easily measurable rates, the D$_2$ conversion being a little faster. It was found, however, that these rates become identical when reduced to equal surface coverage. Again both rates fell in a parallel manner as the surface was poisoned with CO$_2$ to less than 1% of the initial values at 18 $\times$ 10$^{12}$ CO$_2$/cm$^2$.

Both reactions can also be poisoned by lowering the dehydroxylation temperature below 300°C. After pretreatment at 800°C, the site density for the conversion reactions increased to about 30 $\times$ 10$^{12}$ CO$_2$/cm$^2$; that for the exchange reaction fell to about 9 $\times$ 10$^{12}$ CO$_2$/cm$^2$.

Direct measurements of the adsorption of H$_2$ and of D$_2$ were made as a function of temperature, and heats of adsorption were derived therefrom. The heats fell as a function of coverage from about 1.65 to 1.4 kcal/mole for D$_2$ and about 1.5 to 1.3 kcal/mole for H$_2$ respectively as the amount adsorbed varied from 2 to 11 cc(NTP)/g. The coverage
varied from a small fraction (~10^-2) of the number of effective sites at 0°C to several times this number at -195°C. In agreement with this the rates of both conversion and exchange were found to be about first-order in gas pressure at 0°, but nearly zero-order at -195°C.

Arrhenius plots for the H$_2$-D$_2$ exchange were parallel on poisoned and unpoisoned surfaces and indicated an activation energy of about 2.4 kcal/mole. The Arrhenius plots for the conversion reactions were non-linear and varied with the extent of poisoning with CO$_2$. In all cases, however, they converged with the plots for the exchange reaction above -80°C, but curved to lower slopes (lower activation energies) at lower temperatures. Evidently, the conversion and exchange reactions both proceeded by the same dissociative mechanism at high temperatures but only the paramagnetic component of the conversion reaction was significant near the temperature of liquid nitrogen.

If the paramagnetic conversion were effected by unpaired electrons, these should be readily found by EPR if they were present in the concentration indicated by the CO$_2$ poisoning experiments. An extensive search was made, but no signal could be found. Moreover, the site density indicated by these experiments is several orders of magnitude higher than the total metallic impurity content estimated by spark spectral analysis. It is suggested, therefore, that the paramagnetic conversion reactions are catalyzed by exposed Al$_{27}$ nuclei, and several suggestions are advanced as to how this may be possible.
The rate constants for the isomerization of o-xylene over amorphous silica-alumina, several cationic forms of faujasite-type zeolites and hydrogen mordenite have been measured at various temperatures. At a common temperature of 250°C, the rate constants vary over a range of about 20,000 from the least active zeolite (CaX) to the most active (H-mordenite). The hydrogen mordenite is about 135 times as active as the amorphous silica-alumina. However, the most active faujasite-type of zeolite (rare earth H-Y) is only about 40 times as active as amorphous silica-alumina. Thus, in this reaction no "superactivity" of the magnitude claimed for catalytic cracking is observed.

Previous published data on hydrogen-Y, magnesium hydrogen-Y, and rare earth hydrogen-Y zeolites have shown these catalysts to contain 14-18 times as many Bronsted acid sites as does amorphous silica-alumina. It is therefore reasonable to relate the 15-40 fold greater activity of these zeolites to the greater acid site concentration, since xylene isomerization is generally considered to be a proton acid catalyzed reaction. In general, the order of activities of the catalysts studied corresponds to the order of increasing Bronsted acidity.

Whereas the greater activity of some zeolites compared to silica-alumina in the isomerization of xylene is reasonably explained on the basis of relative protonic acid site concentrations, no such obvious relation seems to apply to the cracking of hexane. In the latter case, relative activities of the order of 10,000-20,000 have been claimed for zeolites. A comparison of the data for the two reactions shows that the rate constant for xylene isomerization is one to three orders of magnitude greater than for hexane cracking. Calculations of the activation energy from Arrhenius plots give values of $20 \pm 3$ Kcal mole$^{-1}$ for xylene isomerization compared to about 30 Kcal mole$^{-1}$ for hexane conversion.

It would appear that some other property than protonic acid site concentration is controlling in the cracking reaction. Whether this involves the electrostatic field of the crystal or some other property, such as dynamic variation in acid strength, is not clear at this time. However, since many of the zeolite forms are shown to be less active for xylene isomerization than is amorphous silica-alumina, the factor responsible for "superactivity" is not a universal property of zeolites.
ABSTRACT

THE ISOMERIZATION OF THE XYLENES USING ZEOLITE CATALYSTS

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The isomerization of the xylenes, catalyzed by partially multi-valent metal cation exchanged, partially decationized Type Y zeolite, is invariably accompanied by transalkylation and the extent of isomerization is proportional to the extent of transalkylation. An equilibrium distribution of the xylenes is obtained when over 50% transalkylation has occurred in agreement with calculated values of extent of transalkylation at equilibrium isomerization. Data from the transalkylation of the trimethylbenzene isomers with benzene indicates that this reaction proceeds via a bimolecular mechanism. The products from the transalkylation of both 1,2,3- and 1,3,5-trimethylbenzene and benzene at low conversion contain higher than equilibrium amounts of ortho- and meta-xylene while the product from the 1,2,4-trimethylbenzene reaction contains a higher than equilibrium amount of the ortho-xylene. The low initial concentration of the para-isomer in the product from the isomerization of ortho- and meta-xylene, may be attributed to the greater degree of transalkylation undergone by para-xylene compared to that of the other isomers. Thus, the results obtained from the transalkylation of 1,2,4-trimethylbenzene with toluene show the para-isomer to be initially formed in higher than equilibrium concentrations.

The isomerization of the xylenes via a transalkylation mechanism, involving a diphenylmethane-type intermediate, imposes limitations on the possible isomers that may be derived from the transalkylation reactions. Starting with the meta-isomer, all three trisubstituted isomers may be derived. However, ortho-xylene forms an intermediate which can yield only the 1,2,3- and 1,2,4-trimethylbenzenes, while para-xylene, having four equivalent unsubstituted ring positions, can only yield the 1,2,4-isomer. Using these limitations imposed upon the transalkylated products, the following reaction scheme may be derived.
Such a reaction scheme satisfactorily accounts for the observed results.

The occurrence of the trimethylbenzenes in close to equilibrium distribution indicates the absence of zeolite-hydrocarbon σ-complexes which are known to exist in acid catalyzed systems. The intramolecular mechanism, attributed to the AlCl₃ catalyzed xylene isomerization, might well be a result of the enhanced stability of the meta-xylene and 1,3,5-trimethylbenzene σ-complexes as compared to the corresponding complexes of the other isomers. The principal evidence for the intramolecular isomerization of the xylenes is the apparent absence of direct conversion of the para-isomer to the ortho-isomer and vice versa. However, starting with either of these isomers, the products will be the meta-xylene and the mesitylene σ-complexes until a 1:1 mole ratio of these isomers to the acid catalyst has been established. At this point, equilibration between the acid phase and the hydrocarbon phase will take place and the formation of equilibrium distributions of the isomers will begin in the hydrocarbon phase. Further evidence of a bimolecular mechanism is the observation of second order kinetics in the AlCl₃ catalyzed isomerization of the xylenes in toluene solution. Thus, the transalkylation mechanism, proposed for the isomerization of the xylenes using a zeolite catalyst, may also be operative in an acid catalyzed system but obscured by catalyst-hydrocarbon complex formation.
Catalytic Properties of Hydroxyl Rich and Dehydroxylated LaY*  

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ABSTRACT  

This study deals with the catalytic properties and structure of the rare-earth cation Y zeolites, which are noted for their good structural stability and excellent catalytic activity.

Dehydrated La\textsuperscript{3+}Y and Ce\textsuperscript{3+}Y show no cation-specific C-O stretching frequencies in the infrared spectrum upon carbon monoxide adsorption, indicating the absence of exposed rare-earth cations in the large cavities on the "zeolitic surface" of the crystal. They show, however, two large O-H bands (3640, 3524 cm\textsuperscript{-1}) of similar intensity, which diminish proportionately in Y zeolites with smaller rare-earth cation exchange. The O-H band at 3640 cm\textsuperscript{-1} has the same frequency as the major O-H band found in decationized Y\textsuperscript{*}, and it shows strong hydrogen bonding with water, ammonia, and benzene, suggesting that this OH group is on the zeolitic surface, exposed to reactants entering the large cavities in the zeolite. The O-H band at 3524 cm\textsuperscript{-1}, unique to rare-earth zeolites, does not hydrogen bond with ammonia or benzene, showing that it is in structural positions hidden from the zeolitic surface.

Upon activation at 550°C the surface hydroxyl and the hidden hydroxyl bands appear about equal in size and amount to approximately 0.1 OH per framework aluminum ion. Upon heat treatment at 700°C in vacuum both bands are completely removed (dehydroxylated) and therefore the amount of hydroxyl drops below 0.005 per framework aluminum ion, the level of sensitivity of the infrared technique. Upon addition of water at 100°C both

* In our discussion the Type Y zeolite is designated NaY, see U.S. Patent No. 3,130,007. Forms in which sodium has been exchanged with other cations are designated as Ca\textsuperscript{2+}Y (or Ca\textsuperscript{2+}Y, La\textsuperscript{3+}Y, Ce\textsuperscript{3+}Y), etc. The term "decationized Y" will mean NH\textsubscript{4}Y which was heat treated to decompose the NH\textsubscript{4} ions (see U.S. Patent No. 3,130,006). The type X zeolite is designated X, or NaX, or 13X. (See U.S. Patent 2,882,244).
hydroxyls are regenerated to the original amount. However, no hydroxyl groups are formed in the dehydroxylated zeolite upon treatment with hydrogen, olefins, or paraffin below atmospheric pressure at 300-400°C.

We suggest that upon dehydration the lanthanum ions, two of which take up positions in each of the sodalite units hidden from the zeolitic surface, ionize a water molecule, retaining the O-H (3524 cm⁻¹) group as an electrostatic shield between the two cations, while the proton residue attacks an oxide ion forming a Si⁴⁺ (Al³⁺) O-H (3640 cm⁻¹) linkage on the zeolitic surface. It is probable that upon dehydroxylation the surface hydroxyl group and the proton from the OH in the sodalite unit form water leaving an oxygen-deficient silicon-aluminum linkage on the surface and an oxide ion between the two lanthanum ions.

In the alkylation of toluene by propylene both the hydroxyl rich LaY (activated at 550°C) and the dehydroxylated form (activated at 700°C) have excellent and comparable activities; their activities compare well with that of the decationized Y. The activities to dealkylate cumene are also similar: both the hydroxyl rich and the dehydroxylated LaY have excellent and comparable activity.

The hydroxyl rich LaY has excellent activity for the cracking and isomerization of normal butane, whereas the dehydroxylated LaY has a much lower activity; on treatment with small amounts of water at 450°C the dehydroxylated catalyst attains an activity similar to the hydroxyl rich LaY which was obtained on activation at 550°C.

The catalytic activity for alkylation and dealkylation of aromatics is probably due to similar or even identical centers, which may be either the Lewis acid sites which are already formed in the hydroxyl rich form upon activation at 550°C and are available in high concentration in the dehydroxylated form, or some other sites not identified in the infrared spectrum. In contrast, in the cracking of butane the surface hydroxyls are required in LaY for cracking and isomerization activity.
QUINOLINE TITRATION FOR CUMENE CRACKING ACTIVITY ON MOLECULAR SIEVE CATALYSTS

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We tried to measure the concentration of active sites in molecular sieve cracking catalysts by titrating them with a basic poison. Quinoline was the poison and the catalytic cracking of cumene to benzene and propylene was the indicator reaction. The molecular sieves were type-Y and they were exchanged with either cerium or ammonium ions from their sodium form. We could not find correlations between the experimental titers and either the degrees of ion exchange or the ion exchange capacities of the molecular sieves. However, there was a correlation (1:1) between the experimental titers and the concentration of supercages.

One particular cerium exchanged type-Y molecular sieve had the following composition:

\[(\text{Ce}_{2/3})_{1.08} (\text{Na}_2)_0.10 (\text{Al}_2)_1.00 (\text{SiO}_2)_{5.20}\]

Its quinoline titer was \(3.07 \times 10^{20}\) molecules/gm and the concentration of supercages was \(3.37 \times 10^{20}\)/gm. The concentrations of aluminum atoms and cerium ions were \(22.5 \times 10^{20}\)/gm and \(8.09 \times 10^{20}\)/gm, respectively.

Even though the experimental titers did not correlate with the degrees of exchange in the sieves, it was necessary to ion exchange some cerium or ammonium ion for sodium ions in order to get any cumene cracking. Sodium was exchanged back into an ammonium exchanged sieve in a series of double poisoning experiments. Above a certain critical concentration of sodium ions in the sieve, the quinoline titers declined. Below that concentration the quinoline titers were independent of the sodium. The critical concentration corresponded to the removal of one sodium ion per supercage.

We interpreted these results to mean that a single molecule of quinoline will poison all of the active sites in a supercage, regardless of their number.

The method of poisoning the catalysts and calculating their titers was important. Several studies with the same system: quinoline, cumene and sieves have been reported before, and although the results have been qualitatively similar, there have been quantitative differences. The quinoline titers in this work, that correlated with the concentrations of supercages, were minimum titers for complete poisoning of the cumene cracking activity.
The method of determining a minimum titer involved titrating a catalyst at several temperatures. The temperature range varied from around 300 to 450°C. Higher titers were found at lower temperatures. At the lower temperatures, the endpoints for the titrations corresponded to zero cumene conversion. At the higher temperatures, there was a small but constant residual conversion at the endpoints. The quinoline titer at the highest temperature where residual conversion was still zero was defined as the minimum titer.

We think that the high titers at the low temperatures were caused by adsorption of quinoline in the sieves in excess of that required to poison their catalytic activity. The low titers at the high temperatures were probably due to incomplete poisoning because at the high temperatures, the cumene cracking activity never fell completely to zero.
AN EPR STUDY OF CRYSTAL FIELD INTERACTIONS
ON GROUP IIA-Y ZEOLITES

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The EPR spectra of the adsorbed superoxide ion, $\text{O}_2^-$, and the nitric oxide molecule, NO, were used to determine crystal field interactions on the surface of Group IIA-Y zeolites. Both molecules are especially suited for this type of study since the $2\pi^*$ orbital, which contains the unpaired electron, is degenerate in the absence of any low symmetry crystalline field. If the symmetry about the molecular axis is partially removed, as upon adsorption, one of the $2\pi^*$ orbitals will have a higher energy than the other. This splitting of energy levels is rather strongly exhibited in the $g$ tensor of the EPR spectrum.

The crystal field splitting of the $2\pi^*_{x}$ and $2\pi^*_{y}$ levels was found to vary from 0.3 eV to 0.7 eV, depending on the particular cation and the site which it occupied. Spectra of molecules at two or more different sites were observed for each cation. In contrast to earlier work on decationated zeolites, the spectra of the superoxide ion and the nitric oxide molecule predominantly reflect different sites. For a set of sites which was most clearly seen in the $\text{O}_2^-$ spectra, the strength of the crystal field interaction increased from Ba through Ca but then decreased for Mg. The Mg may have been present as Mg(OH)$_2^+$. No aluminum hyperfine interaction was observed in the spectra for this set. Another site, which was more clearly seen in the NO spectra, was similar to that previously detected on decationated Y zeolites. This site appeared to involve an aluminum atom as indicated by the hyperfine structure. The concentration of these sites increased as one moved up the series from Ba through Mg.

The concentration of all paramagnetic species was found to be in the range from $10^{17}-10^{18}$ spins/g which is considerably less than was found for the decationated form. The superoxide ion, however, does not give as reliable an estimate of the site concentration as the nitric oxide molecule since the number of ions formed is a function of the type of irradiation, the irradiation dosage, and the dose rate. The paramagnetic nitric oxide species did not require irradiation.

From the catalytic work of other investigators it has been suggested that strong electrostatic fields, which increase from Ba through Mg, are responsible for the activity of these zeolites. It has also been
proposed that hydroxyl groups are made more acidic by neighboring cations. Alternately, the present EPR work supports the thesis that the catalytic activity can be more closely related to a defect site similar to that envisaged for the decationated zeolite. The role of the divalent cation is in the formation and stabilization of the defect site. The lower catalytic activity of the Group IIA zeolites, when compared with decationated zeolites, may be only the result of a lower concentration of sites.

This work does confirm that a number of different adsorption sites exist on the Group IIA zeolites and that each of these sites is characterized by a relatively strong crystal field interaction with the adsorbed ion or molecule.
Studies of the Catalytic Dealkylation of Ethyl Acetate

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The homogeneous, vapor phase decomposition of ethyl acetate to acetic acid and ethylene is known to proceed by an intramolecular mechanism involving intermediate formation of a six-membered ring ("cis-elimination"). Almost no work has been reported on the possibility of a solid-catalyzed dealkylation of carboxylic acid esters. We have now found that the dealkylation of ethyl acetate can be catalyzed by a number of refractory oxides, ranging in nature from alumina to synthetic zeolites.

The studies reported here were conducted in a continuous flow system rather than a pulsed micro-catalytic reactor, since we were initially more interested in steady state behavior than in initial deactivation. Liquid ethyl acetate was introduced continuously, from a glass syringe driven by a motorized syringe pump, into a heated vaporizer where it was mixed with nitrogen carrier gas. Reactor effluent was passed through two traps in series, one at 0° and the other at -78°C. Liquid condensate (acetic acid plus unconverted ethyl acetate) was analyzed in a gas chromatograph equipped with a Polypak-1 column. Uncondensed effluent (ethylene plus nitrogen) was also analyzed by gas chromatography with a silica gel column.

The catalyst charge was 20 cm³ in all cases. The catalysts examined were commercial materials, obtained through the courtesy of the manufacturers. Convenient test conditions were found to be in the temperature range of 265° to 275°C and a space time (based on empty reactor at temperature) of 0.6 to 0.7 sec. Catalysts were normally pre-dried at 275°C in flowing nitrogen; on occasion a higher pretreatment temperature was studied. Control experiments in which the reactor was packed with glass beads showed that under the normal test conditions, negligible vapor phase dealkylation of the ethyl acetate occurred.

There was a general correlation of steady-state dealkylation activity of the catalyst with catalyst acidity. In one series of tests the activity increased in the order \( \text{Al}_2\text{O}_3 < \text{SiO}_2 - \text{Al}_2\text{O}_3 \) (Houdry Type S-46) < \( \text{SiO}_2 - \text{Al}_2\text{O}_3 \) (Houdry Type S-65) < \( \text{SK}-500 \) (Linde). SK-500,
the most active catalyst tested in these experiments, is a Type Y synthetic zeolite that has been partially decationized and partially ion exchanged with rare earth metal ions. In another series with Type Y zeolites containing different cations, the order of increasing activity was Na-Y < Ca-Y < H-Y (ex NH₄-Y) < SK-500. Interestingly, the hydrogen form of a mordenite-type zeolite, Zeolon H (Norton), was somewhat less active for this dealkylation reaction than H-Y and much less active than SK-500. Coke deposition over SK-500 was much lower than over H-Y, although the conversion over SK-500 was almost two-fold higher. Significant deactivation was observed over a 1-1 1/2 hour period for all of the more active zeolites; after this time, conversion was reasonably steady-state.

Computations, by Wheeler's method, of pore diffusional limitations indicated that substantial all (> 95%) of the macropore surface of the zeolites was effectively used even in the case of SK-500, the most active catalyst. This was confirmed by the fact that a reduction in granule diameter for SK-500 by a factor of about four resulted in no significant increase in conversion. Neither the computation nor the granule diameter study is informative in deciding whether micropore diffusion may be a slow step. From a theoretical standpoint, one does not know what value to use for the diffusivity in the micropores; from an experimental standpoint, it would be necessary to study granules made from individual zeolite particles of differing size.

The activity of SK-500 after regeneration at 450°C. was found to be substantially less than that of fresh catalyst. This unexplained effect was not the result simply of heating at 450°C., since fresh catalyst pre-dried at 450°C. was even more active than that pre-dried at 275°C. Moreover, treatment of the regenerated catalyst with a moist air stream at 325°C. did not result in any improvement.

The data obtained to date suggest that the reaction is acid-catalyzed. The reason for the higher activity of SK-500 relative to H-Y remains undetermined, however, and may be associated with specific cation effects. The relatively low activity of Zeolon H is interesting; a plausible explanation may be advanced on the basis of relatively easy plugging of the non-intersecting channels in the mordenite structure.
Acid catalysis of the dealkylation could occur by a unimolecular (El) mechanism involving formation of a carbonium ion intermediate. It is planned to investigate this possibility by studying the dealkylation of higher esters such as butyl or pinacolyl acetate.
THERMAL BEHAVIOR OF FAUJASITE

by W. J. Ambs and W. H. Flank

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Little precise data are available concerning the high-temperature thermal behavior of the synthetic faujasite crystal structure, although semi-quantitative and qualitative observations have been made. A method is described which allows fairly precise determination and intercomparison of thermal stability data in terms of the structural breakdown temperature found by differential thermal analysis.

Data are presented to show that the thermal stability of faujasite is dependent on the level of sodium present. Using either conventional exchange techniques or the intermediate calcination procedure described by McDaniel and Maher, the same simple relationship was found between the sodium content of ammonium-exchanged faujasite and the temperature at which breakdown of the zeolite structure occurred. This relationship extends to sodium contents below 0.1%, and demonstrates the existence of a continuum of properties for variously-exchanged faujasite samples.

X-ray diffraction analysis shows that, regardless of the degree of sodium removal or the method of exchange employed, the faujasite structure is retained to just below the breakdown temperature. Material heated just beyond the breakdown temperature exhibited no crystallinity, and material heated further, to beyond the mullitization temperature, contained crystalline mullite. Samples prepared by different exchange methods down to the same sodium level, and then calcined and scanned under identical conditions, showed very small differences in the x-ray peak intensity distribution, and in the lattice parameter. However, significant differences, indicative of structural changes, appeared when a sample was evaluated before, and after, calcination at 540°C.

Based on the data obtained, thermally-induced migration of cations is postulated as the mechanism for a process resulting in facilitation of further exchange. A general discussion of aluminosilicate structure degradation is presented. Mechanistic proposals are made to account for kinetically-controlled thermal destruction at all levels of sodium concentration, as well as other observed and postulated phenomena relating to thermal stability.