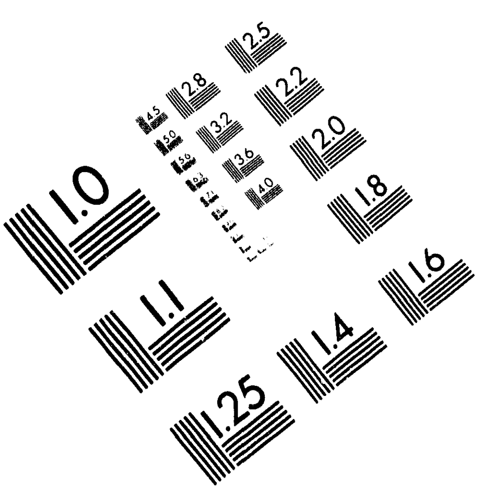
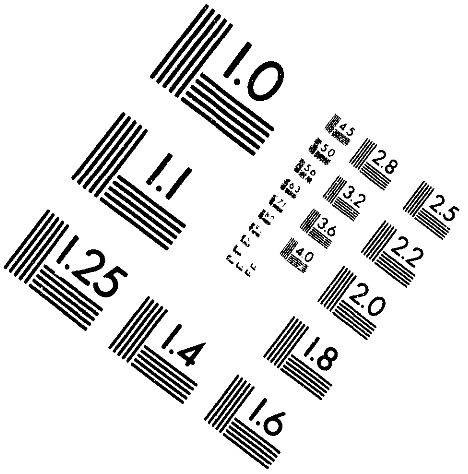


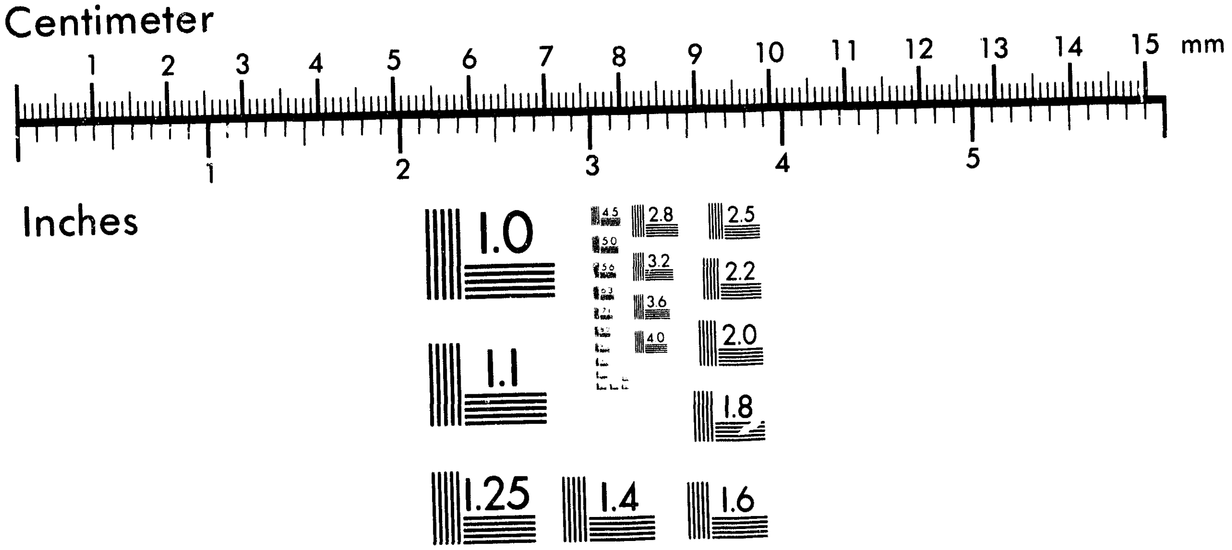
AIIM

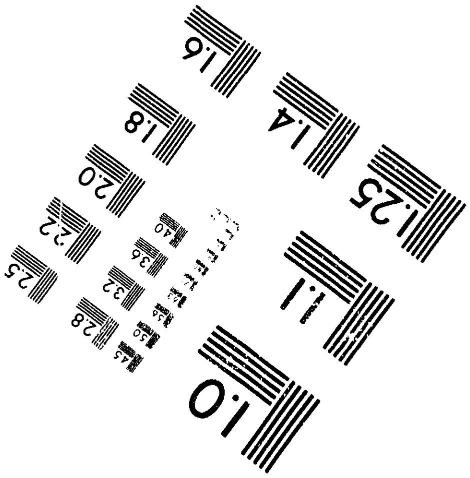
Association for Information and Image Management

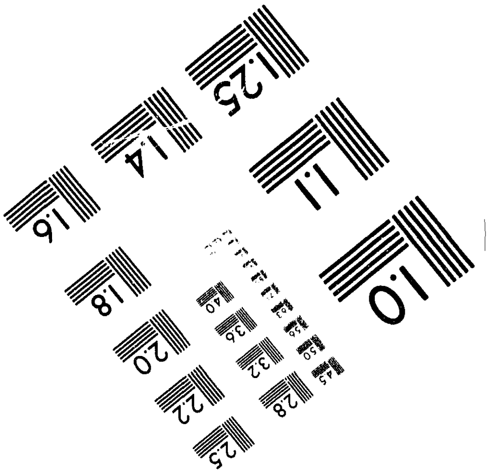
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

DOE/ER/13183--9

Progress Report: July 1, 1993 - June 30, 1994
Thermodynamic and Kinetic Aspects of Surface Acidity
(DE-FG02-84ER13183)
J. A. Dumesic
Chemical Engineering Department
University of Wisconsin, Madison, WI 53706

During the past year, our research funded by the Department of Energy has involved studies of solid acidity, the role of acidity in methylamine synthesis reactions, and catalytic cracking of hydrocarbons. The objectives of our work are to understand the factors controlling the type and strength of acid sites on surfaces and to quantify the kinetic aspects of the catalytic cycles in which these acid sites participate. The combination of results from these efforts leads to identification of possible strategies to develop new generations of solid acids with specific catalytic properties for clean and effective chemical manufacturing.

Surface Acidity Studies

Our work to characterize solid acidity has utilized the adsorption of base probe molecules, as studied using such techniques as microcalorimetry, infrared spectroscopy, and temperature-programmed desorption. Microcalorimetric measurements of differential heats versus adsorbate coverage provide information about the distribution of acid site strengths, infrared spectroscopic studies probe the nature of the acid sites, and temperature-programmed desorption spectra under conditions where readsorption is fast give insight into the free energy of desorption. Our studies have also employed NMR spectroscopy to investigate the environment and chemical bonding of deuterons associated with Brønsted acid sites. Solid acid catalysts that we are studying include various zeolites, amorphous silica/aluminas, and alumina doped with controlled amounts of basic metal oxides. For these latter materials, we are also studying catalyst basicity using the above approach for adsorbed acidic molecules, such as carbon dioxide.

During the past year we completed our studies of the acidity of ZSM-5 catalysts, in which we explored the effects of non-framework aluminum species on the acidity of Brønsted acid sites associated with the framework (1). We also finished a study in which we verified that microcalorimetric

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

studies of ammonia adsorption at 423 K can, in fact, be used to determine acid strength distributions of high surface area catalysts (2). In more recent work, we also investigated the effects of Sn^{2+} and Sn^{4+} cations on the acid and base sites of alumina (3). We found that Sn^{2+} cations neutralize the acid and base sites of alumina, while Sn^{4+} cations have only a minor effect on the acidic properties of alumina. The primary implications of this work are that the tin/alumina system is acidic under oxidizing conditions, while it possesses very few acid or base sites under reducing conditions.

Our studies of the acid/base properties of metal oxides continued with microcalorimetric and infrared spectroscopic measurements of the effects of adding potassium, magnesium and lanthanum oxides onto alumina (4). Microcalorimetric measurements of NH_3 adsorption at 423 K showed that addition of basic metal oxide cations at loadings less than 200 μmol/g converted the stronger acid sites (heats from 140-160 kJ/mol) to sites of intermediate strength (100-140 kJ/mol). Increasing the loadings of the basic oxides further eliminated the stronger acid sites and eliminated sites of intermediate strength. Infrared spectra of adsorbed NH_3 showed that γ-Al_2O_3 contained both Brønsted and Lewis sites after calcination at 723 K, and addition of potassium removed Brønsted acid sites. The addition of basic metal oxides at loadings less than 500 μmol/g increased the number of weak basic sites (heats from 60-100 kJ/mol) and sites of intermediate strength (100-140 kJ/mol). Strong basic sites (140-160 kJ/mol) were formed at higher loadings of basic oxides on alumina. The order of effectiveness in the neutralization of acid sites and the formation of new basic sites was $MgO < La_2O_3 < K_2O$, and this order is also the order of decreasing Sanderson electronegativity. Thus, our systematic studies of the acid/base properties of metal oxides are showing trends that can be used to formulate materials with desired surface properties.

Another aspect of our studies during the past year was the synthesis of Mg-Al-O hydrotalcites and the use of these materials as basic catalytic materials following calcination at elevated temperatures (5). These materials had been synthesized in the literature using alkali metal hydroxides, and the resulting catalysts were claimed to be strongly basic. We found, however, that the basicity of these compounds was caused by the alkali metal cations remaining on the surface. In our work, we developed a procedure for synthesis of alkali-free Mg-Al-O hydrotalcite compounds using ammonium hydroxide. We characterized our materials using X-ray diffraction, ^{27}Al NMR, and microcalorimetric and infrared spectroscopic studies of NH_3 and CO_2 adsorption. These materials display weak acid and basic sites at low Mg/Al ratios, while these materials show moderate basicity at high Mg/Al ratios. In no cases were these materials as basic as pure MgO. Thus, compounds prepared from Mg-Al-O hydrotalcites do not possess strong basic sites in the absence of alkali metal cations. As such, these materials will find applications as high surface area catalysts for reactions requiring moderate to weak acid/base properties.

In a related work we have been studying the acid/base properties of europium oxides on silica and alumina. These oxides are basic, and they were chosen as important model compounds because europium cations can be characterized in detail using both Mössbauer and luminescence spectroscopies. During the next year we plan to use these materials to explore the factors that control the formation and strength of basic sites on mixed-metal oxides.

Adsorption and Synthesis of Methylamines

During the past year we have completed our microcalorimetric studies of the adsorption of the reactants and products of methylamine synthesis (6). The differential heat of adsorption versus coverage on H-ZSM-5 and H-mordenite exhibits two plateaus for adsorption of NH_3, monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), and dimethylether (DME). The high heat of adsorption for these molecules corresponds to adsorption on Brønsted acid sites, while the lower heat corresponds to non-specific adsorption. The heat of adsorption on the Brønsted acid sites correlates linearly with proton affinity of the base for NH_3, MMA, DMA, and DME, while the heat of adsorption of TMA is lower than expected from this correlation. The heats of adsorption of water and methanol are lower than for the amines, consistent with the low proton affinities of these species.

We have also consolidated our kinetic studies of methylamine synthesis and the following related reactions: methanol dehydration to dimethylether, monomethylamine disproportionation, reactions of monomethylamine with methanol and dimethylether, dimethylamine disproportionation, and reactions of dimethylamine with methanol and dimethylether (7). In short, methylamine production was first order in ammonia; however, the reaction was positive- or negative-order in methanol, depending on the catalysts studied. DME production was inhibited by increasing ammonia partial pressures but was generally first order in methanol. Methanol dehydration is first order with respect to methanol pressure. The rate of DME formation in the absence of amines is considerably faster than the rate under methylamine synthesis conditions. Disproportionation reactions of MMA and DMA are fast compared to the rate of methyamine synthesis. In situ IR studies show the presence of methoxyl species under methanol dehydration conditions, and the surface appears to covered primarily by adsorbed amines during methylamine synthesis and amine disproportionation conditions.

Our results suggest that methoxyl species are involved in methanol dehydration to DME, and these species are apparently blocked by adsorbed ammonia or amines. During methylamine synthesis, strongly adsorbed ammonia and amines are methylated by reaction with weakly adsorbed methanol and dimethylether. Disproportionation reactions occur by exchange of methyl groups between strongly and weakly adsorbed amines. A critical aspect of this cycle is that the combination of acid sites and weak adsorption sites is desirable for methylamine synthesis and related reactions, *i.e.*, acid sites are required for the reaction steps and weak sites are required to facilitate desorption of strongly adsorbed amines from the acid sites.

We are currently in the process of bringing together the results of our microcalorimetric studies, infrared spectroscopic measurements, and reaction kinetics studies to formulate a quantitative description of the factors controlling methylamine synthesis and related reactions over acid catalysts. This description will allow us to elucidate ways by which the product selectivity for methylamine synthesis reactions may be controlled and to allow us to determine how these reactions may be used to probe surface acidity.

Hydrocarbon Cracking over Y-zeolite-based Catalysts

Our recent studies of catalytic cracking have involved development and calibration of a kinetic model to analyze isobutane cracking over acidic Y zeolites (8,9). Our model is based on carbenium ion chemistry and incorporates initiation, oligomerization, β-scission, olefin desorption, isomerization, and hydride-transfer processes. Kinetic data were collected at Engelhard Corporation using a plug-flow reactor.

Our analyses of isobutane cracking indicate that different catalytic cycles can be operative at different points of a PFR. Catalytic cycles that include initiation and olefin desorption are dominant at the entrance of the reactor and low conversions, while catalytic cycles that include oligomerization, β-scission, and hydride-transfer reactions become dominant at the latter stages of the reactor and at high conversions. Initiation reactions leading to olefin production are irreversible and a weak function of conversion. Hydride-transfer reactions are mostly irreversible and are responsible for paraffin production. However, these reactions are a strong function of the residence time of carbenium ions on the surface. The paraffin-to-olefin ratio is a strong function of the ratio of the rates of hydride-transfer reactions to initiation reactions.

Our results indicate that reducing the acidic strength of the catalyst by steaming decreases the rates of initiation reactions, as well as reducing the rates of hydride-transfer reactions by decreasing the residence time of the carbenium ions. The latter effect dominates, and the paraffin-to-olefin ratio decreases with catalyst steaming.

During the past several months we have worked to extend our understanding of isobutane cracking to describe the activity and selectivity of isoheptane cracking over several steamed, Y-zeolite-based catalysts (10). Importantly, the chemistry of this reaction is essentially the same as the chemistry of isobutane cracking. The main differences between the mechanisms for isobutane and isoheptane cracking are due to the longer carbon chain of isoheptane, which leads to additional reaction pathways. For example, cracking at the terminal C-C bond yields methane, and leaves a primary carbenium ion on the surface that rearranges to a tertiary ion. In addition, the longer carbon chain makes possible the production by initiation reactions of higher paraffins like ethane, propane, isobutane, and n-butane. Furthermore, the species that can undergo β-scission and hydride-transfer reactions are different for isoheptane, although the chemistry of these reactions does not change. In particular, isobutane and isohexane, in addition to propane, n-butane, and isopentane, can be formed by hydride transfer from a tertiary position on the reactant paraffin to a surface carbenium ion.

In short, we have found that catalytic cycles for isobutane cracking involving initiation reactions are independent of conversion, while cycles that include hydride transfer, oligomerization, and β-scission reactions become more important at higher conversions. Accordingly, higher conversions cause a decrease in olefin selectivity. Because of the larger number of reaction pathways available for isoheptane cracking, paraffins and olefins with three or more carbon atoms can be produced by cycles that include both initiation and hydride-transfer reactions. The paraffin-to-olefin ratio can not be greater than unity, and the effect of conversion on this value is smaller than for isobutane cracking (10).

We suggest that kinetic models based on the fundamental surface chemistry believed to control catalytic cracking processes can be used to identify similarities in the reactivities of different hydrocarbon molecules. Any fundamental differences in reactivity due to effects of hydrocarbon size or structure can then be ascertained. This approach provides strategies to develop new catalysts that utilize this surface chemistry effectively to increase the formation of a desirable compound or to reduce the production of pollutants. This will be a direction for further research in our group.

Future Research

Our future work will continue to deal with the factors controlling the activity and selectivity of catalytic processes over acid sites. We will continue our studies of the acid/base properties of mixed metal oxide catalysts. Systematic trends in the behavior of these materials are beginning to emerge, allowing us to address the goal of synthesizing mixed-metal oxides catalysts with desired acid/base properties.

We will continue our studies of zeolite acidity through the use of ^{2}H solid-state NMR. This technique allows us to study the motion of the acidic deuterons; specifically, variable-temperature experiments will be used to determine the energetics of the motion. We believe that this information, combined with the analysis of the type of motion, can then be correlated to the strength of solid acids.

Our kinetic studies of isoheptane cracking over Y-zeolite-based catalysts will continue. Our results to date have provided key insight into the quantitative aspects of the catalytic cycles involved in the cracking of this molecule. Our future work will explore how the acidity and structure of the catalyst affect the relative rates of these catalytic cycles and thereby control the activity and selectivity of the catalyst.

We are currently extending our work to so-called super-acid materials, such as antimony halides and oxides of iron, tin, and zirconium treated with sulfur oxides. Studies of these first three elements will be complemented with Mössbauer spectroscopic characterization of the acid sites.

The catalytic applications of solid super-acids are numerous, and our work for next year will focus on isomerization of n-butane at low temperatures. We are currently preparing catalytic materials, and we are modifying a catalytic reactor for kinetic studies of this reaction. We will characterize these catalysts with the combination of chemical and physical techniques that we have developed in our previous work on surface acidity. In addition, we hope to be able to extend our knowledge of catalytic cycles operative during hydrocarbon cracking over Y-zeolite-based catalysts to quantify differences in the behavior of super-acid catalysts from conventional, strong acid catalysts.

References

1. Thermogravimetric and Microcalorimetric Studies of ZSM-5 Acidity, Catalysis Letters, **18**, 183 (1993), with M. R. Gonzalez, S. B. Sharma and D.T. Chen.

2. Microcalorimetric Studies of Ammonia Adsorption on γ-Al_2O_3, HNa-Y Zeolite, and H-Mordenite, accepted in Catalysis Letters, with B. E. Spiewak, B. E. Handy, and S. B. Sharma.

3. Microcalorimetric and Infrared Spectroscopic Studies of γ-Al_2O_3 Modified by Tin Oxides, accepted in Catalysis Letters, with J. Shen, Chen Yi and R. D. Cortright.

4. Microcalorimetric and Infrared Spectroscopic Studies of γ-Al_2O_3 Modified by Basic Metal Oxides, submitted to Journal of Physical Chemistry, with J. Shen, Chen Yi and R. D. Cortright.

5. Synthesis and Acid/Base Properties of Magnesium-Aluminum Mixed Oxides Obtained from Hydrotalcites, submitted to Langmuir, with J. Shen, J. M. Kobe, and Yi Chen.

6. Methylamine Synthesis over Solid Acid Catalysts: Calorimetric and Infrared Spectroscopic Studies of Adsorbed Species, Journal of Catalysis, **146**, 257 (1994), with D. T. Chen, L. Zhang and Chen Yi.

7. Methylamine Synthesis over Solid Acid Catalysts: Reaction Kinetics Measurements, submitted to Journal of Molecular Catalysis, with D. T. Chen, L. Zhang, J. M. Kobe, and Chen Yi.

8. Isobutane Cracking over Y-zeolites: Part 1. Development of Kinetic Model, submitted to Journal of Catalysis, with G. Yaluris, J. E. Rekoske, L. M. Aparicio, and R. J. Madon.

9. Isobutane Cracking over Y-zeolites: Part 2. Catalytic Cycles and Reaction Selectivity, submitted to Journal of Catalysis, with G. Yaluris, J. E. Rekoske, L. M. Aparicio, and R. J. Madon.

10. Catalytic Cycles and Selectivity of Hydrocarbon Cracking on Y-zeolite-based Catalysts, submitted to Industrial and Engineering Chemistry Research, with G. Yaluris, R. J. Madon and D. F. Rudd.

DATE FILMED

6/22/94

END

4