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Selectivity in Catalysis

Mark E. Davis, EDITOR
California Institute of Technology

Steven L. Suib, EDITOR
University of Connecticut

Developed from a symposium sponsored
by the Catalysis and Surface Science Secretariat
at the Fourth Chemical Congress of North America
(202nd National Meeting of the American Chemical Society),
New York, New York,
August 25–30 1991

American Chemical Society, Washington, DC 1993

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Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

M. Joan Comstock
Series Editor

Preface

AN EMPHASIS ON SELECTIVITY in this volume relates to increasing research in homogeneous catalysis and areas that bridge many fields of chemistry. The symposium on which this book is based is an outgrowth of the Catalysis and Surface Science Secretariat of the American Chemical Society and several divisions—the Divisions of Colloid and Surface Chemistry; Fuel Chemistry; Industrial and Engineering Chemistry, Inc.; Inorganic Chemistry, Inc.; Petroleum Chemistry, Inc.; and Physical Chemistry. A goal of the symposium was to assemble researchers from chemistry, chemical engineering, materials science, and related areas concerned with enhancement of selectivity in catalysis.

This book deals with four major areas of selectivity: stereoselectivity; clusters, alloys, and poisoning; shape selectivity; and reaction pathway control. An overview of the book and reviews of each of the four major areas are included as introductory chapters. Each review is followed by individual contributions by attendees of the symposium.

We thank Susan Lambert, secretary general of the Catalysis and Surface Science Secretariat, for her efforts in organizing sponsorship of this symposium. We also thank the attendees, the authors, and the American Chemical Society.

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September 1, 1992

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Selectivity in Catalysis

An Overview

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This review encompasses the general area of selectivity in catalysis as well as the four major specific areas discussed in this book; Stereoselectivity; Clusters, Alloys and Poisoning; Shape Selectivity; and Reaction Pathway Control. Examples are taken from the literature for each of these four areas of recent articles that focus on selectivity in catalytic reactions. Specific reviews of the four areas listed above can be found in the overview chapters by D. Forster and coworkers, K. J. Klabunde, M. E. Davis and coworkers; and H. C. Foley and M. Klein.

I. INTRODUCTION

This review is an overview of recent literature research articles that deal with selectivity in catalysis. Four specific areas including stereoselectivity; clusters, alloys and poisoning; shape selectivity; and reaction pathway control will be discussed. This review is not meant to be a complete discussion of these areas. It represents a small fraction of the research presently underway and a very minor fraction of the available literature in this subject. The order of topics will follow the four major areas outlined above, however, there is no particular order for the articles discussed in each section.

Selectivity in catalysis is one of the most important factors to be controlled by researchers. Selectivity can be controlled in several ways such as by structural, chemical, electronic, compositional, kinetic and energy considerations. Certain factors may be more important in homogeneous catalytic reactions rather than heterogeneous reactions and vice versa. In most cases, however, little distinction will be made regarding the control of product selectivity for these two major types of catalysts.

Selectivity in catalysis might be controlled by preparation and use of new materials such as new zincosilicate molecular sieves such as VPI-7 having 3 membered rings,[1] gallophosphate molecular sieves with 20 atom ring pore openings having cloverleaf shaped windows,[2] 3 ring zeolitic ZSM-18 type materials,[3] clays pillared with metal oxide clusters,[4] and perhaps soccerball shaped C_{60}, C_{70} buckeyball cage structures.[5]

Besides new materials, it may be possible to modify surfaces of existing materials to provide sites to enhance selectivity. Considerable research has been

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done in the area of molecular recognition at interfaces to control both chemical and physical properties of resultant materials. Such tailor-made surfaces can be used to control crystal nucleation, polymorphism, optical birefringence and nonlinear optical properties and the structure of materials.[6]

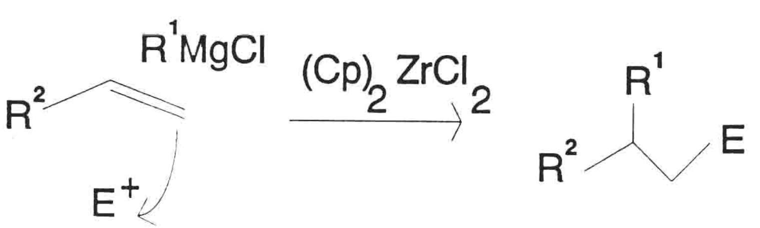
Control of pore sizes of known catalysts like zeolites has been known for some time although the use of chemical vapor deposition (CVD) of organosilanes to control pore sizes has been the focus of recent research.[7] Other catalysts like silica have been treated with methods like CVD and sol-gel in order to deposit thin films. Monolayer coatings of titanium oxide prepared by sol-gel methods have been recently used to coat silica and such films are active in alcohol dehydrogenation reactions.[8]

Finally, new methods of analysis have recently been developed that may allow characterization of single atoms on surfaces such as atomic force microscopy.[9] In certain cases, in situ experiments can be done such as the study of electrodes, enzymes, minerals and biomolecules. It has even been shown that one atom from a tip can be selectively placed on a desired surface.[10] Such processes may one day be used to prepare catalysts that may enhance selectivity. Other methods that show promise as regards detection of surface catalytic intermediates are temperature programmed desorption techniques.[11] Selective poisoning of some surface intermediates with monitoring via temperature programming methods may also allow the preparation of more selective catalysts.

Such speculation suggests a tremendous potential for continued developments in the area of selectivity enhancement in catalysis. The remainder of this review focuses on current literature concerning selectivity in catalysis.

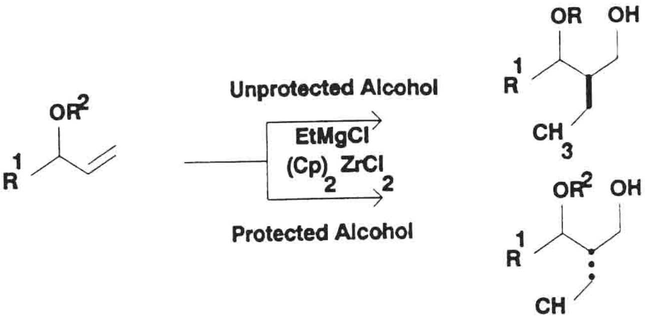
II. STEREOSELECTIVITY

Stereoselectivity in homogeneous catalytic reactions is well documented. Oftentimes mechanisms can be postulated regarding individual steps in contrast to heterogeneous systems. A recent detailed investigation of the stereoselective formation of C-C bonds catalyzed by $(C_5H_5)_2ZrCl_2$ has been reported by Hoveyda and Xu.[12] The initial step in these reactions is the addition of an alkyl Grignard reactant to an unactivated olefin followed by further bond formation as in Equation (Eq.) [1]:[12]



[1]

The above reactions are one pot syntheses, can be used for double alkylation or hydroxyalkylation of alkenes in good (55-65 %) yield, and with outstanding regiocontrol (> 99 %). Diastereochemical control in the formation of allylic alcohols and ethers has been shown to proceed with even better yields (up to 92 %) although the stereocontrol is somewhat decreased (95:5, highest; as low as 67:33) due to the use of THF as a solvent which can influence the stereochemistry. These studies are important since the different reaction pathways can lead to both protected and unprotected alcohols. Such pathways are shown in Eq. 2.[12]



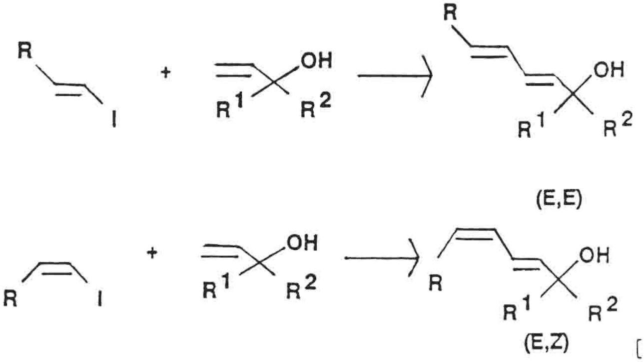
[2]

Both syn and anti carbometalation products were prepared with excellent stereochemistry in the above reactions. The role of solvent was not well studied, however, it is clear that stereocontrol is influenced in these systems by the nature of the solvent. It was suggested that a 16 electron intermediate zirconocene [$(Cp)_2Zr$] species is the active catalyst in such systems.

Giles and coworkers have recently reported the use of $TiCl_4$ in CH_2Cl_2 at -78°C for the stereoselective isomerization of naphthyl- and phenyl-dioxolanes to yield pyrans that are important in aphid pigments.[13] Other Lewis acids besides $TiCl_4$ such as BF_3, $SnCl_4$, $Ti(IsoPr)_2Cl_2$ and $Ti(IsoPr)_3Cl$ are not effective in such reactions. ^1H NMR and nuclear Overhauser effect spectroscopies were used to establish stereochemistry. Some diol side product (13 %) was also formed. The major effort in this research was to clearly identify products of the isomerization.

The preparation of highly chemo-, regio- and stereo-selective (E,E) and (E,Z) conjugated dienols important in several biological systems such as leucomycins and oxazolomycins has been reported by Jeffery.[14] These homogeneous reactions were done in the presence of different silver salts and palladium acetate catalysts. These reactions were highly dependent on the nature of the solvent but also dependent on the nature of the silver salt. Silver carbonates, nitrates and acetate salts gave conjugated diols with yields from 60 to 82 % with either (E,E) or (E,Z) type double bonds. The role of the anion of the silver salt was not studied in any great detail. The process was reported to be generally useful for primary, secondary and tertiary allylic alcohols.

A general scheme for the formation of (E,E) and (E,Z) conjugated diols is given in Eq. 3.[14] In the following scheme (Eq. 3) R = C_6H_{13}, R^1 is either H or CH_3, and R^2 can be H, C_2H_5, C_5H_{11} or CH_3.

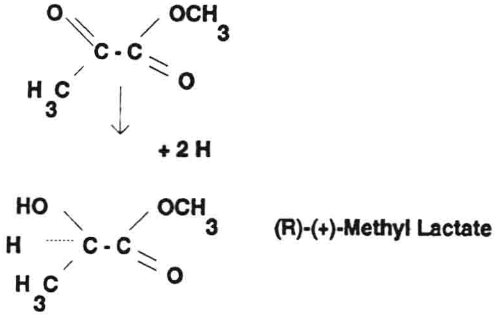


[3]

Biocatalysts such as Candida cylindracea lipase enzymes have recently been used in enantioselective hydrolyses of racemic esters by Fowler, Macfarlane and Roberts.[15] The (R,R) diastereoisomer was the main product (91 +/- 0.5 %) as determined by NMR spectroscopic analysis of the products. These authors point out the difficulty of measuring such diastereoisomer ratios by using NMR methods, however, their results show a clear selectivity towards the (R,R) diastereoisomer.

Sutherland, Ibbotson, Moyes and Wells have published a detailed account of the heterogeneous enantioselective hydrogenation of methyl pyruvate ($CH_3COCOOCH_3$) to R-(+)-methyl lactate over Pt/silica surfaces modified by sorbed cinchona alkaloids.[16] Kinetic, isotherm and molecular modeling calculations were used to develop an idea of the role of the cinchonidine modifier. This system is quite unusual; high enantioselectivity is achieved only with Pt, only in the presence of cinchonidine modifiers and only for the hydrogenation of α-ketoesters.

The order of reaction for methyl pyruvate was zero and for hydrogen was unity indicating that the ketoester is strongly adsorbed and the hydrogen is weakly adsorbed. By assuming that hydrogenation occurs via addition of two H atoms from below the plane of the adsorbed methyl pyruvate, the configuration outlined in Eq. 4[16] (which generates the major product (R)-(+)-Methyl Lactate) is necessary since its mirror image leads to the formation of (S)-(-)-Methyl Lactate.



[4]

Molecular modeling studies suggested that the lowest energy configuration of sorbed cinchonidine was a structure where the two aromatic rings were parallel to the Pt surface in a close-packed array. The quinuclidine groups of cinchonidine lie above the Pt thereby leaving access for sorption of methyl pyruvate in a unique surface orientation. The authors stress the importance of using a well known catalyst/support system and have carried out several other experiments to suggest that the high enantioselectivity is limited to date to the above system.

A final example of a stereoselective heterogeneous catalytic system is the work of Laycock, Collacott, Skelton and Tchir.[17] Layered double hydroxide (LDH) synthetic hydrotalcite materials were used to stereospecifically polymerize propylene oxide [PO] to crystalline isotactic and liquid atactic poly(propyleneoxide) [PPO]. These authors suggest that the LDH surface acts as other inorganic or organometallic coordination initiators or catalysts by providing specific surface orientations for propylene oxide monomer. X-ray powder diffraction showed some loss of crystallinity after calcination and X-ray photoelectron spectroscopy showed an enhancement of Mg/Al content due to restructuring of the Mg and Al surface atoms. The surface was also rich in Cl^-

(anion precursor) as well as carbonate ions which have been shown to incorporate into LDH materials during synthesis.

No characterization of the catalysts after reaction was reported. Detailed ^{13}C NMR analyses were used to identify structures in the PPO products. A mechanism involving ring opening of PO after coordination of a PO monomer to the surface of the LDH leading to discrete sterically hindered catalytic sites was invoked to explain the high stereodirecting influence of the mixed oxide catalyst.

There are clearly some interesting observations reported in the above papers[12-17] that seem to pervade stereoselective reactions. First of all, the nature of the solvent in homogeneous stereoselective reactions is critical. Secondly, unique steric requirements for reactants on solid surfaces appear to lead to enhanced stereoselectivity. Thirdly, modifiers and promoters in both solution phase and solid phase catalysis appear to have marked effects on product selectivity.

III. CLUSTERS, ALLOYS AND POISONING.

Clusters and alloys are molecular species that may show different catalytic activity, selectivity and stability than bulk metals and alloys. Small metal clusters and alloy clusters have been studied recently for potential use as catalysts, ceramic precursors, and as thin films. Several fundamental questions regarding such clusters are apparent. How many atoms are needed before metallic properties are observed? How are steric and electronic properties related to the number, type and structure of such clusters? Do mixed metal clusters behave like bulk alloy phases?

A major focus of our research program has been the preparation of small (< 5 Å) Co, Fe and Fe/Co alloy clusters in zeolites.[18] Catalytic reactions of cyclopropane and hydrogen over such clusters have shown that turnover frequencies are 3 orders of magnitude lower for the isomerization of cyclopropane to propylene than for bulk (>20 Å) Co particles supported on Al_2O_3. Such clusters are selective towards propylene at temperatures of 120°C and towards propane via hydrogenation at 160°C as the cluster size grows to 10 Å size particles. Further sintering at 180°C leads to 15 Å particles on the surface of the zeolite as well as a shift in products to methane and ethane. Such structure sensitive reactions with rates measured as a function of particle size clearly show that Co clusters have different structural, catalytic and physical properties than bulk Co metal or large Co particles on various supports.

Another focus of this section involves the role of poisons in catalysis. In general, poisons are impurity species that decrease the selectivity towards a desired product. In the area of fluid cracking catalysis, metal poisons or contaminants in the feed deposit on the zeolite/matrix fluid cracking catalysts (FCC) and can cause severe changes in activity and selectivity. For example, we have shown that vanadium poisons decrease the activity of FCC materials almost immediately by destroying the structure of the Y zeolite portion of the FCC even at 1 ppm levels of vanadium.[19] Nickel poisons on the other hand, lead to overcracking of gasoline to light gases. Several methods have been used to prevent such poisoning such as demetallization and addition of passivating agents to the catalyst.

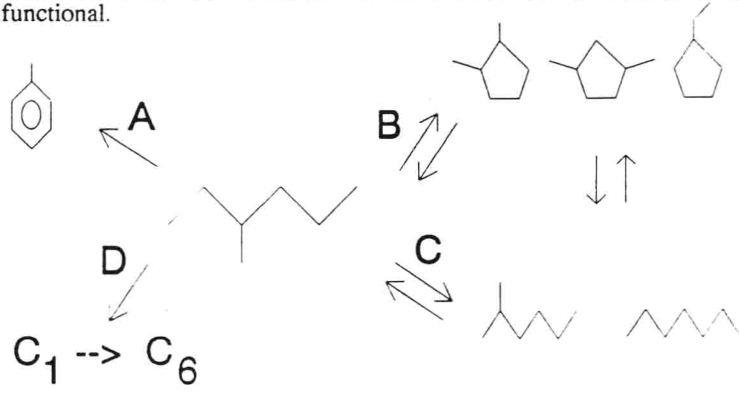
Pine has recently focused on the role of vanadium in the destruction of USY zeolite.[20] Kinetic studies of the reaction of vanadium and steam (used in catalyst regeneration) have been carried out for vanadium levels of 0-4000 ppm and at temperatures of 740 to 800°C. Kinetic data suggest that vanadium acts as a catalyst for the breakdown of the zeolite lattice via a solid state mechanism.

Further studies showed that vanadium also attacks silicalite implying that framework decomposition occurs via Si-O bond breakage. The rate limiting step of the destructive role of vanadium was proposed to be the attack of vanadium on surface hydroxyl groups.

Espeel, Tielen and Jacobs have recently shown that metal clusters in zeolites can be used in electron transport chain conversions of ethylene to acetaldehyde in an analogous fashion to that of homogeneous Wacker catalysts.[21] The electron transport chain involves transfer of electrons from ethylene to the metal clusters to oxygen. Infrared, kinetic and isotope labeling studies were done that suggested an electron transfer mechanism first involving coordination of ethylene to Pd^{2+} followed by an intramolecular hydrogen transfer leading to the production of acetaldehyde. The combination of Cu^{2+} and Pd^{2+} leads to a synergistic effect with overall activity increased by a factor of 5. Advantages of such a system are the avoidance of high chloride concentrations as in homogeneous solution which leads to incorporation of Cl- in products and use of solid acids rather than highly acidic solutions.

The role of iron clusters in Fischer-Tropsch catalysis has been the focus of considerable studies. Cagnoli et al. have recently studied the role of Fe clusters on silica and alumina supports for methanation.[22] Chemisorption, catalysis and Mössbauer spectroscopy experiments were used to study the effect of dispersion and the role of various supports. Although several oxidation states of iron were observed, the focus of this research was on Fe clusters which were found to be on the order of 12 Å crystal size. The authors proposed that metal support interactions were greater for silica than alumina supports and that selectivity differences between these catalysts were due to differences in surface properties of silica vs. alumina. Differences in selectivity for Fe/SiO_2 catalysts at different H_2/CO ratios were attributed to differences in coadsorption of H_2 and CO. Selectivity differences are difficult to explain in such systems even when only one metal is present.

Normand et al. have studied Pd deposited on several metal oxide supports in reactions of methylcyclopropane hydrogenolysis, 3-methylhexane aromatization, and in Fischer-Tropsch catalysis.[23] Three classes of oxides were studied, those that were not reducible such as Re_2O_3, those with anion vacancies produced during reduction like CeO_2, and those with intrinsic anion vacancies such as nonstoichiometric Pr_6O_{11} and Tb_4O_7. Hydrogenolysis reactions were found to occur on Pd sites whereas aromatization reactions were believed to be bifunctional.



[5]

Reactions of 3-methylhexane were found to occur on the support alone which complicated the above studies. Besides aromatization to toluene (A), isomerization to cyclopentane derivatives (B), isomerization to heptane and other branched hexanes (C) and cracking to C_1 to C_6 hydrocarbons (D) were all observed as depicted in Eq. 5.[23]

For aromatization, the following order of decreasing activity in aromatization was observed for the supports themselves:

$$Al_2O_3 > PrO_x > CeO_2 > TbO_x > La_2O_3 > Nd_2O_3$$

The Pd/Al_2O_3 system and Pd/PrO_x systems were studied in more detail than the others and kinetic and thermodynamic results suggest that the Pd/PrO_x catalysts have a much higher density of specific sites (about 1.6 times) for aromatization than on the alumina support.

Effects of additives are often difficult to unravel, perhaps because they serve more than one role in catalytic reactions. Nitta, Hiramatsu and Imanaka have suggested recently that Cl^- additives in the hydrogenation of cinnamaldehyde and crotonaldehyde over supported Co catalysts serve to enhance selectivity by influencing both the hydrogen reduction and hydrogenation steps in these reactions.[24] Crystallite sizes of cobalt are markedly influenced by the nature of the cobalt anion precursor ranging from < 40 Å for acetate precursors to 180 Å for chloride precursors as determined by X-ray line broadening experiments. The other role of Cl- anions is to decrease the hydrogenation of C=C double bonds during hydrogenation of cinnamaldehyde and crotonaldehyde. Anions, mean crystallite sizes, initial selectivities and selectivities at 50 % conversion are summarized in Table I.[24]

The above studies show that Cl- anions may play several roles in enhancing the selectivity in such reactions. A maximum in both selectivity and activity was found when the Cl/Co ratio was 0.2. Studies with various supports suggested that metal support interactions were also important.

A final example of the role of additives is that of Larkins and Nordin.[25] Li_2CO_3 when added to MgO catalysts increases the selectivity to C_2 hydrocarbons in oxidative coupling reactions of methane as has been found by others. Catalytic, scanning electron microscopy, X-ray powder diffraction, temperature programmed reactions and electron microprobe studies have been used to show that additives of both Zn and Mn can enhance selectivity to C_2 hydrocarbons in these systems.

If Mn additives are added at too high a loading (8%) then selectivity to C_2 hydrocarbons is lowered and total oxidation prevails. Catalytic data are summarized in Table II[25] for such systems.

These data show that small amounts of Mn (0.1 mol %) incorporated into Li/MgO considerably enhance the selectivity to C_2 hydrocarbons. Additives of Zn also enhance the C_2 selectivity, however, not as significantly as Mn dopants.

In the absence of Li, the Mn doped materials produce a significant amount of CO and CO_2. In the absence of Li, the Zn doped materials primarily yield CO_2. As temperature is lowered from 805°C to 710°C the overall conversion is decreased as expected and it may be difficult to make valid comparisons for catalysts having significantly different conversions. Nevertheless, these data suggest that the role of additives can markedly influence selectivity as was observed in other systems noted above. The exact role of Li, Mn and Zn in these systems is not well known.

There are several features of the different systems described above for the cluster, alloy and poisoning section that are common. First of all, the structural