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"Gheorghe Asachi" Technical University of Iasi, Romania

Book Review

HANDBOOK OF HETEROGENEOUS CATALYSIS

Second, Completely Revised and Enlarged Edition
Volume 7

Gerhard Ertl, Helmuth Knözinger, Ferdi Schüth, Jens Weitkamp (Editors)
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The seventh volume of the **Handbook of Heterogeneous Catalysis** deals with *Organic Reactions* and it is organized in 17 sub-chapters.

The sub-chapter *Aromatization of Light Alkanes* briefly reviews the relevant reactions of aromatization of light alkanes in the range C_3-C_8 with focusing on Ga/HZSM-5 and Pt/KL catalysts. Their synthesis and mechanisms proposed for the reactions occurring in the case of each catalyst are also presented. Finally, recent developments regarding industrial applications are illustrated, as well.

The chemistry of the *Opening of Aromatics* is quite complex but it can be reduced at two main steps; hydrogenation of the aromatic ring to cycloalkanes followed by hydrodecyclization reaction. Due to the fact that ring hydrogenation is a fairly advanced sub-field of heterogeneous catalysis, this sub-chapter is focused on the hydrodecyclization reactions. The relevant mechanisms of cycloakane hydrodecyclization are discussed. This will form the basis for reviewing the recent literature on the ring opening of (i) multi-ring (mainly bicyclic) aromatics in diesel and jet fuels, (ii) one-ring aromatics in gasoline without degradation of carbon number and (iii) one-ring aromatics occurring in pyrolysis gasoline followed by hydrocracking into a mixture of ethane, propane and n-butane which is an excellent synthetic feedstock to steam crackers.

The alkylation of aromatic compounds is widely used in the large scale synthesis of petrochemicals and in a great variety of fine chemicals and intermediates processes, which is the topic of the third sub-chapter, *Alkylation of Aromatics*.

General mechanistic and kinetic principles of the alkylation of mononuclear alkylbenzenes are taken into consideration as well as the synthesis of the most important alkylbenzenes, phenols and anilines. The sub-chapter ends with a review on the synthesis of the binuclear aromatics, i.e. alkylated naphthalenes and biphenyls.

The isomeration and translakylation as well as the synthesis of alkylaromatics via alkylation evolved as an efficient means of producing purified base aromatics as the demand for synthetic fibers grew. Due to their importance, the sub-chapter *Isomerization and Translakylation of Alkylaromatics* provides an up-to-date review of the catalysts, processes and mechanisms of the alkylaromatic transformations.

The chemical industry uses alkanes as feed materials for chemicals and provides a cheaper alternative to acetylene or even olefins. Their main drawback is the low reactivity. Consequently, the catalytic conversion of alkanes and especially of methane to more useful chemicals and fuels is one of the major challenges for heterogeneous catalysis in the 21st century. Hence, the sub-chapter *Non-Oxidative Activation of Alkanes* deals with the activation of the most challenging alkanes such as methane, ethane, and propane.

Classical solutions involve processes operating under severe conditions but the side, unwanted effects cannot be avoided. A more selective activation of alkanes under non-oxidative conditions requires special, high-performance catalysts which are also stable at higher temperatures necessary for favorable thermodynamics. The potential of these activation methods for the production of chemicals from alkanes has not been fully realized and is the main focus of this sub-chapter.

Light alkenes are among the most important intermediate products in the chemical industry and they are mainly obtained as by-products of refinery or petrochemical operations. In this context, the sub-chapter *Dehydrogenation of Alkanes* provides useful information on reaction conditions, catalytic systems, kinetics and mechanism as well as the adequate reactors for light alkane deghydrogenation.

The commercially available processes for light alkane dehydrogenation such as Oleflex and Pacol processes (UOP), STAR process (Uhde), CATOFIN process (ABB Lummus) and FBD process (fluidized bed dehydrogenation) are also discussed herein.

The sub-chapter *Dehydrogenation of Ethylbenzene* deals with the ethylbenzene dehydrogenation as important heterogeneously catalyzed reaction for production of styrene. Briefly introduction to thermodynamics of the reaction and the resulted by-products is offered. Catalysts, with accent on the role of potassium and iron oxide based systems are nicely presented nearby to the bibliographic references.

The sub-chapter *Methatesis of Alkenes* provides useful information on the scope of this reaction as well as a detailed analysis on the catalytic systems, mechanism and kinetics. The commercial processes which use solid metathesis catalysts are also discussed.

The sub-chapter *Dehydrogenation of Alcohols: Formaldehyde* introduces some specific features of the catalytic dehydrogenation of primary and secondary alcohols to corresponding aldehydes and ketones.

Particular interest is assigned to direct dehydrogenation of methanol to formaldehyde. Therefore, a good review including a detailed discussion on this topic is found herein. Special attention is offered to silver, copper, and zinc based catalysts although other useful catalysts are presented, as well. Few industrial applications available today makes the subject of the concluding part of this sub-chapter.

The sub-chapter *Selective Hydrogenation of Hydrocarbons* is concerned with the kinetics and the mechanisms of selective hydrogenations of alkadienes and cycloalkadiens. Another topic is related to hydrogenation of ethyne, which shows some specific features such as the formation of unsaturated oligomers, so-called green oil. Comparison between catalytic properties of palladium and platinum are also provided; furthermore, the effect of the particle size of supported metals on activity and selectivity is considered.

Chemical engineering aspects of selective hydrogenation are also found in the book. The partial hydrogenation of benzene to cyclohexene, introduced as an industrial process in 1990 is treated, as well. Finally, the sub-chapter ends with the industrial applications of selective hydrogenation in downstream processing of naphtha cracking effluents.

The aim of the sub-chapter *Regioselective Hydrogenations* is the reviewing some recent and important developments in the field of regioselective hydrogenations with heterogeneous catalysts, which are usually supported metal catalysts and, to a much lesser extent oxides (e.g. in transfer hydrogenations). Selectivity as a function of catalytic reaction engineering aspects (process parameters, reaction kinetics, mass and heat transport, reactor design) are also considered.

Some of the factors controlling the intramolecular selectivity, i.e. the preferred hydrogenation of one functional group compared with another of a molecule with conjugated double bonds, are well understood and presented in the book beside to certain reactions.

The sub-chapter *Selective Oxidations* gives a look inside of the oxidation reactions such as hydrocarbon oxidation, oxidative dehydrogenation of alkanes, oxyfunctionalization of alkanes, oxyfunctionalization of alkyl aromatics, direct ring oxidation of aromatics to phenols, alkene epoxidation, acetoxylation of ethylene, oxidation of low-molecular-weight hydrocarbons, ammoxidation, ammoximation, oxidation of alcohols with molecular oxygen, phenol hydroxylation and related oxidations. Detailed mechanisms, kinetics as well as catalytic systems are presented for each of these reactions.

The sub-chapter *Amination Reactions* focuses on the heterogeneously catalyzed reactions of ammonia and amines with a wide variety of organic reactants. Comprehensive reviews previously prepared on this topic as well as the immense number of patents, indicating the synthetic value and industrial importance of catalytic amination are referred herein.

The sub-chapter *Halogenation Reactions* deals with the halogenations (fluorination, chlorination, bromination, iodination) over solid heterogeneous catalysts such as silica, alumina, chromia, activated carbon and zeolites. A summary of these reactions (up to the end of 1994) including reactant/halogenating agent, product, catalyst and remarks is provided.

The sub-chapter *Acylation of Aromatics* refers to the heterogeneous catalyzed acylation of aromatics and different topics are addressed: (i) the zeolite-catalyzed acylation of aromatics, (ii) catalysis by (modified) ordered mesoporous materials, (iii) sulfated zirconia type catalysts, (iv) heteropolyacid catalyzed acylation of aromatics, (v) catalysis by activated clays and (vi) Nafion type catalysts.

The sub-chapter *Elimination and Addition Reactions* presents few theoretical features of these two types of reactions including thermodynamics, mechanism, the influence of the reactant structure, catalysts and kinetics followed by some practical applications among them dehydrochlorination, dehydration, hydrochlorination, hydration and amination, and addition of alcohols and organic acids to alkenes.

The sub-chapter *Stereoselective Reactions* briefly overviews on the approaches applied to design solid, enantioselective catalysts as well as on the application of chirally modified metal hydrogenation catalysts that represents, as yet, the only synthetically useful approach in heterogeneous enantioselective catalysis. The interest is directed on the developments acquired during the past 10 to 15 years.

The sub-chapter *Miscellaneous Catalytic Systems* treats different topics such as hydroformylation on solids catalysts, Wacker chemistry with solid catalysts, oxidations on immobilized molecular catalysts, and chemicals from carbon dioxide.

Brandusa Dragoi
Cezar Catrinescu
Faculty of Chemical Engineering
and Environmental Protection
"Gheorghe Asachi" Technical University
of Iasi, Romania