

A Specialist Periodical Report

Catalysis

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A Review of Recent Literature

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Preface

Catalysis research continues to address both the traditional areas of chemical synthesis and fuel production, but with increased emphasis on environmentally benign processes and products. This volume reflects the interest in both. The reviews provided here include hydrogen production, upgrading of fuels to minimize emissions, as well as new catalysts and processes for chemical synthesis – each with attention to the environmental impact of catalyst activity and selectivity.

Mehri Sanati and Mostafa Faghihi (Växjö University, Sweden), Bjorn Harrysson (Nynäs Naphthenics AB, Stockholm, Sweden), Bjorje Gevert (Chalmers Gothenburg, Sweden), and Sven Järås (KTH, Stockholm, Sweden) provide a review of hydrodearomatization, which is important in fuel processing. This reaction is typically carried out with other hydrotreating reactions (*e.g.*, hydrodesulfurization). Hydrodearomatization is essential in order to improve the fuel quality and minimize undesirable emissions. One key area for research is sulfur tolerance, particularly for the noble metal-based catalysts. The authors explore the reactivity of a wide range of catalysts, and address the hydrodearomatization of mono- and multi-ring aromatic compounds.

Wolfgang Hoelderich and Felix Kollmer (University of Technology, RWTH, Germany) examine catalytic oxidations for fine chemical synthesis, which typically use oxidizing agents other than dioxygen, such as N_2O and H_2O_2 . The authors point out the important differences between oxidation reactions (and catalysts) needed to produce bulk chemicals, compared to those needed to produce fine chemicals: operating temperature, reactor design.

In another review from KTH, Johan Agrell, Bård Lindström, Lars Pettersson, and Sven Järås review the catalytic generation of hydrogen from methanol. This is one of the options for generation of hydrogen from liquid fuels for stationary and mobile applications, fuel processing, and fuel cells. Methanol can be used to generate hydrogen by several reactions: decomposition to CO and hydrogen, steam reforming, and partial oxidation (as well as combinations of these reactions). The authors explore the different catalysts needed for each of these reactions, as well as recent industrial research activity.

Tomoyuki Inui (Air Water Inc., Osaka, Japan) also addresses reforming of hydrocarbons for syngas and hydrogen production. His review focuses on the reaction of methane with CO_2 , oxygen and/or steam. There are significant research needs in this well-studied area, including coke formation and reactor design/kinetics. Both noble metal and conventional Ni-based catalysts are reviewed, as well as new synthesis techniques.

Olga Buyevskaya and Manfred Baerns (Institute for Applied Chemistry

Berlin-Adlershof, Germany) provide a thorough review of the oxidative functionalization of ethane and propane. This review concentrates on the oxidative dehydrogenation of these two compounds to produce the corresponding olefins. In addition, the selective oxidation of ethane and propane to produce directly higher value oxygenates such as acetic acid, acrolein and acrylic acid is addressed.

Wataru Ueda (formerly at Science University of Tokyo in Yamaguchi; now at Hokkaido University, Sapporo, Japan) and Sui Wen Lin (Tokyo Institute of Technology, Japan) also address selective oxidation of lower alkanes – epoxidation, coupling and dehydrogenation reactions, for example. Their review focuses on the use of metal halide catalysts for these reactions. These catalysts can increase the activity and selectivity of selective oxidation reactions. Particular emphasis is given to the layered metal chloride catalysts for selective oxidations.

Sung-Won Ham (Kyungil University, Korea) and In-Sik Nam (Pohang University of Science and Technology, Korea) discuss the selective catalytic reduction of NO_x using ammonia over conventional vanadium-based catalysts, zeolite catalysts, and exploratory catalysts based on novel titania formulations and pillared clays. A comprehensive review of poisoning and deactivation is also provided, along with a study of the mechanism/kinetics and reactor modeling.

Finally, Chunshan Song (Penn State University, USA) reviews the conversion of polycyclic hydrocarbons into specialty chemicals over zeolites. Until recently, the conversion of these compounds into useful products was not widely studied. These compounds are used in advanced polymers, but the large-scale production of the corresponding monomers requires selective catalysts for the conversion of polycyclic aromatic hydrocarbons. This review focuses on the various zeolites that can be modified to produce these compounds.

I am working with the authors of Volume 17 to prepare reviews of topics that are at the leading edge of catalysis research. I look forward to bringing this next volume to you. As always, comments are welcome.

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Catalytic Hydrodearomatization

BY MEHRI SANATI, BJÖRN HARRYSSON, MOSTAFA FAGHIHI,
BÖRJE GEVERT, AND SVEN JÄRÅS

1 Introduction

Hydroprocessing of various feeds for the production of fuels is extensively practised in the petroleum industry, and to some extent in coal liquefaction and in the upgrading of synthetic fuels and lubricant oils. Another promising area where hydroprocessing can be applied is the development of renewable non-fossil fuels (pyrolytic bio-oil) for the elimination of the oxygen-containing molecules and the improvement of the H/C ratio.

Hydroprocessing reactions occur on the active sites of the catalysts. Also, a suitable pore size distribution of the catalysts is required to ensure the access of reactant molecules to the active sites. The catalysts used in hydroprocessing consist of a molybdenum catalyst that is supported on a high surface area carrier in the 100–300 m²/g range, most commonly alumina, and is promoted by either cobalt or nickel. The concentration by weight of the metal is usually 1–4% for Co and Ni, and 8–16% for Mo.¹ The catalysts are active in the sulfided state, being either presulfided or sulfided on stream with a sulfur containing feed. Monometallic (Pt or Pd) and bimetallic (Pt–Pd) catalysts of noble metal supported on γ -Al₂O₃ are known to be highly active in the hydrogenation of aromatics under mild conditions. However, noble metal catalysts are easily poisoned by a small amount of sulfur; severe pre-treatment of the feedstock is needed to reduce sulfur to a few ppm. Recent studies have dealt with how to improve the activity of these catalysts and their sulfur tolerance, *e.g.* by adding a second transition metal or using different support material.^{2–11}

The typical feedstock for laboratory tests is usually either a mixture of model mono-compounds and/or a mixture of different aromatic hydrocarbons.^{12–13} In industrial feeds, however, several types of aromatics are present, whose hydrogenation activities differ considerably. The composition and concentration of various nitrogen and sulfur compounds also significantly influence the activity.

The process is normally carried out in a trickle-bed reactor at an elevated temperature and hydrogen pressure. In the case of severe deactivation, an ebullating bed reactor might be used but this type of reactor is not suitable due to back-mixing when a high conversion is needed. The specific characteristic of a trickle bed reactor is that a part of the catalytic surface is covered by a liquid

and the other part by a gas. In the common set up, the liquid phase flows downwards through the reactor concurrently with a gas phase that partly consists of vaporized compounds. The temperature and pressure ranges for the hydrogenation of aromatic hydrocarbons in a liquid phase batch reactor were reported to be 450–700 K and 3.5–17 MPa, respectively.^{14–25,12–13}

Hydroprocessing catalysts are quite versatile, exhibiting activity for a number of important reactions. Those of major interest in hydroprocessing that might be referred to as hydrotreating correspond to removal of heteroatoms; hydrodesulfurization (HDS), hydrometallization (HDM), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). These reactions involve hydrogenolysis of C-heteroatom bonds. The removal of sulfur and nitrogen is necessary to meet environmental limits. Sulfur may also cause problems with catalyst poisoning and corrosion. HDN is needed to avoid catalyst poisoning of acid sites and improving stability in lube oils.

An important reaction in petrochemical industry and refineries is hydroconversion, which enables a change in the molecular weight and structure of organic molecules. Examples are hydrogenation (HYD) and hydrodearomatization (HDA). When oil is hydrotreated, the reduction of aromatic compounds competes with the removal of sulfur and nitrogen. The purpose of hydrotreating (in the latter sense) is to improve the stability and quality of the product. The reduction of aromatic compounds, especially polyaromatics, gives a higher stability to the product, as well as affecting the solubility and colour of the product. Aromatics in fuels not only lower the quality and produce undesired exhaust emissions, they also have potential hazardous and carcinogenic effects.²⁶ Thus polyaromatic compounds are removed to meet health and environmental regulations. The growing understanding of health hazard associated with these emissions is leading to limitation in the use of aromatics in both Europe and the United States.²⁷

The process to make cleaner fuels that are more environmentally friendly is often accompanied by desulfurization and hydrodearomatization. Decreasing the aromatic content increases the cetane number in diesel fuel.

Two approaches, a single-stage process and a two-stage process, have been proposed for distillate fuels (particularly diesel fuels) to meet these strict standards for diesel fuels. The single-stage process combines severe hydrodesulfurization and hydrogenation using a single conventional sulfided CoMo, NiMo or NiW catalyst. In order to reach the necessary aromatic saturation the H_2 pressure needs to be substantially higher than the H_2 pressure at which current hydrodesulfurization units operate.²⁸

The two-stage system uses a conventional hydrotreating catalyst in the first reactor and a noble metal catalyst in the second; this yields a low aromatic diesel stream at moderate hydrogen pressure.^{29,30}

This latter system is highly active for the reduction of aromatics but is very susceptible to sulfur poisoning; the sulfur concentration at the inlet of the second reactor must be reduced to a few parts per million.³¹

Thus, the use of these catalysts depends strongly on severe pre-treatment conditions, unless the sulfur tolerance can be greatly improved for the noble

metal catalyst. A number of recent studies have attempted to address this problem by developing catalysts with a high resistance to the sulfur poisoning and at the same time retaining a high hydrogenation activity.

In spite of the large number of articles published in recent years, the subject has been widely reviewed. The catalytic aspects of the hydrogenation were discussed by Krylov and Navalikhina.³² Special attention to the preparation methods was discussed in more detail by P. Grange and X. Vanhaeren.²⁷ A comprehensive review of the hydrodeoxygenation, with particular focus on upgrading of bio-oils, was published by Furimsky.³³ Catalyst deactivation during hydroprocessing, including the adverse effects of the O-compounds, was reviewed by Furimsky and Massoth.³⁴

In this review, the primary focus is on the most recently reported work in the literature for both basic and industrial aspects of hydrodearomatization reactions. It is an extension and update of recent studies dealing with the aromatic reduction in different petrochemical feedstocks. These reviews, which have recently appeared in literature, provide comprehensive information regarding hydrodearomatization.^{31, 35–37}

A comprehensive review of the reactions during hydroprocessing has been published by Topsøe *et al.*¹

2 Hydrogenation of Mono-, Di-, Tri-, Multiring and Mixtures of Aromatic Compounds

In recent years an increasing awareness of the use of aromatics contained in different feedstocks, especially distillate fuel (in particular diesel and gas oils), with respect to the adverse effects of undesired emissions and potential health risks, has received considerable attention. In addition, a high aromatic content is associated with poor fuel quality, giving low cetane number in diesel fuel and a high smoke point in jet fuel.

To date, a number of the model compounds that are representative of components in industrial feeds, have been extensively studied on several catalysts. These include both unsupported and $\gamma\text{-Al}_2\text{O}_3$ supported hydrogenation catalysts, using the conventional CoMo, NiMo, NiW, and platinum group metals (including ruthenium, rhodium, palladium and platinum). On all catalysts, the rate of hydrogenation generally increases with the number of aromatic rings present, *i.e.* a low rate of hydrogenation is observed for mono-aromatic rings such as benzene.¹ The greater reactivity for hydrogenation with higher fused ring systems, such as naphthalene and anthracene, is due to the fact that the resonance energy of the second ring of these multiple compounds is less than for benzene.³⁵

Table 1 of this review shows the recent related publications on hydrodearomatization and the catalytic systems, reaction conditions and product selectivities for these studies. The choice of model compounds were often the mono-aromatics compounds or a mixture of the aromatics in order to simulate a composition similar to the industrial feedstock in refinery.