

Air pollution prevention and sustainability - the role of catalysis

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1 Introduction

Catalysis is an effective technology that plays a major role in preventing the pollution of our environment now and in the future. NO_x, SO_x, VOCs, CO, CH₄, N₂O, automotive exhaust gases, O₃, and CO₂ can be converted either to less harmful compounds or valuable products by catalytic processes. A major opportunity exists to discover a single catalyst composition that can be used for a wide spectrum of compounds existing in flue and exhaust gases. For example, in automotive exhaust catalysis, a two stage catalyst is a short term solution, but a single catalyst would be much better. The future focus for diesel emissions is on NO_x removal and treatment of particulates via post treatment. The effect of greenhouse gases (CO₂, CH₄, N₂O, CFC) can be diminished in the future by e.g. reducing the energy consumption, by photocatalysis and by catalytic production and pollution abatement technologies. CO₂ can be captured by chemical solvents, physical absorption, by cryogenic methods and membranes and by physical adsorption. Captured CO₂ can be further used as a green, versatile and low price C1 carrier in chemicals and fuels production, e.g. in methanol, DMC, DME, carbonic esters syntheses. (Ballivet-Tkatchenko et al. 2006, Centi & van Santen 2007, Halmann & Steinberg 1999, Jenssen & van Santen 1999).

Reuse of different by-products from chemical industry, odor control and toxic waste gas purification are areas where catalytic processes are playing even a more important role nowadays. There are still many opportunities for innovations, improved understanding, and above all fundamental understanding of these new processes. The manufacture and use of catalysts for environmental protection is conducted more scientifically and in a more sophisticated manner than was done some years ago.

Catalysts play an essential role in the refinery (also biorefinery) and chemical industries and in pollution prevention. Their role is going to increase in forest industry because of the biorefinery approach. Both economic and environmental issues are driving the changes behind process improvements in catalysis and in new catalyst development. New catalysts are designed to increase the reaction yield, enhance selectivity and rate, reduce production of unwanted by-products and pollutants, and to increase life-time of catalysts.

Catalysts for environmental protection will show the greatest growth in demand. This is due to industry-wide changes required for protection of the environment and more stringent regulations. Particular emphasis will be paid to the use of catalysis in addressing environmental issues such as the need to clean polluted waste streams and stack gas emissions, to increase process efficiency, to reduce hazardous by-products, and to utilize biomass in chemicals, fuels and energy production, i.e. to develop and take into use the biorefinery concept or at least parts of it in different branches of industry.

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2 Theory behind catalysis

A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction. A catalyst can also be defined as a substance that increases the rate of a reaction without being appreciably consumed in the process. It is a substance that in small amounts causes a large change in the reaction rate and selectivity. (Thomas & Thomas, 1997, Richardson 1989).

Environmental catalysis has been defined as the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic syntheses of important compounds without the formation of environmentally unacceptable by-products (Centi et al. 2002). The role of environmental catalysis has grown tremendously during the past 20 years and today environmental catalysts are considered to be the biggest group of catalysts used industrially, the other groups being catalysts used in chemical, polymer and refinery industry.

Catalysts are composed of three main types of components, i.e. active components (metals, semiconducting oxides or sulfides and insulators), a support or a carrier, and promoters and inhibitors. The following basic principles are met in catalysis. The reaction equilibrium is unchanged. The catalyst promotes only those reactions for which the Gibbs free energy change is less than zero. Since the equilibrium constant K is unchanged, the catalyst accelerates both the forward and reverse reaction rates. A catalyst, in principle, promotes only one of the possible reactions, leading to improvements in selectivity and activity. Ideally, a catalyst remains unchanged in the reaction but in real use catalysts suffer from irreversible or reversible chemical and physical changes. Thus, activity, selectivity and stability are the most important properties of catalysts. (Richardson 1989).

3 Catalysis and Sustainability

According to the Brundtland report (Brundtland report 1987) sustainable development is defined as the development that 'satisfies the needs of the present without compromising the ability of the future generations to meet their own needs'. Sustainable production is the creation of goods and services using processes and systems that are non-polluting, conserving of energy and natural resources, are economically efficient, safe and healthful for workers, communities, and consumers, and socially and creatively rewarding for all working people (Lowell Center for Sustainable Production 2009). The sustainability targets can be gained by intensifying and focusing the research in e.g. catalysis to the following areas (Centi and Perathoner 2008, Clark 1999, Ehfeld et al. 2000, Kiwi-Minsker & Renken 2005, Somorjai 2004):

- Improving the integration of hetero-, homo- and bio-catalysis,
- Making steps forward to bridge the gap between surface science and theoretical approach and applied catalysis,
- Improving understanding of the catalytic chemistry and dynamics in operating conditions,
- Exploring catalysis in combination with energy sources other than thermal,
- Developing selectivity of multi-step reactions, and
- Integrating catalyst and reactor design via taking into account the advances in microreactor technology and phenomena integration.

In process development, environmental, health, safety and economic targets favor ideal processes, which have maximum atom economy, are safe and simple and are approaching 100% yields in only a few process steps (Pereira 1999). Efficient use of resources and waste minimization, i.e. materials efficiency, are typical targets of sustainable process design.

In sustainable production and energy, the goal is to e.g. minimize energy use, waste generation and environmental hazards, and improve process safety. This approach is called the Green chemistry and engineering approach (Anastas & Warner 1998, Anastas & Williamson 1998, Anastas et al. 2001). Green chemistry and engineering have sets of principles that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and application of chemical products. Green chemistry and engineering incorporate pollution prevention practices in the manufacture of chemicals and other products.

4 Future Challenges

Nanostructured catalytic materials are seen to offer excellent ways to enhance sustainable use of catalysis. They have benefits such as better control of activity, selectivity, and deactivation of catalysts. Recent advances have been the design, synthesization, characterization, and manipulation of nanoscale catalysts. Research in catalysis nanoscience has dealt with the relationships between catalyst synthesis and active site structure on the atomic- and nanoscale, reaction mechanisms, and catalyst activity, selectivity, lifetime. These advances have led to the design of catalysts for novel catalytic reactions that take advantage of self-assembly of catalytic sites in predetermined two- and three-dimensional configurations. This has a great impact on chemicals manufacturing in the future both from environmental and economic perspectives, allowing design of catalytic materials from the atom-scale via combining the best features of biocatalysis, homogeneous and heterogeneous catalysis into the same pot, e.g. a catalyst and a reactor. This also offers new tools to process design via process integration at the nanoscale. (Grunes et al. 2003, Somorjai 2004, Zhou et al. 2004).

In attempts to bridge different catalysis areas from biocatalysis to homogeneous and heterogeneous catalysis, the goal is to combine the high selectivity of homogeneous cluster catalysts with the stability and versatility of supported heterogeneous catalysts (Grunes et al. 2003, Somorjai 2004). Catalysis by nanomaterials is optimized to direct the chemical transformation of raw materials into desired products via sustainable production methods. This way of acting will offer the possibility to go to more sustainable approaches in chemicals and products manufacturing, distribution, and use in our society in the near future.

Catalysts have an enormous impact on chemical industry, transportation, energy production and everyday life via enabling reactions to take place, via making processes greener and more efficient, via making processes environmentally friendly, more economic (e.g. a 0.5% to 1% increase in selectivity can lead up to a million Euro increase in the operating profile in a company), and inherently safe. Environmental catalysis has continuously grown in relevance over the last two decades, but especially the area of interest for research has rapidly expanded. From the traditional areas of NO_x and VOC control, research activities have extended to a wide range of applications including lowering of the environmental and energy impact of refinery and chemical production, and improvement of eco-compatibility of non-chemical productions and transport. In all these applications catalysis is the essential tool to enable a sustainable production and transportation.

The innovations in the fields of process and environmental catalysis and the highlights for the new directions for research driven by market, social and environmental needs are seen in the following areas (e.g. Centi 2002, Centi and Perathoner 2008):

- Catalysis for energy-friendly technologies and processes (primary methods),
- New advanced clean-up catalytic technologies for industry, transportation and indoor air quality (secondary methods),
- Catalytic processes and technologies for reducing the environmental impact of chemical and agro-industrial wastes and improving the quality and reuse of water (secondary methods),
- Catalytic processes for sustainable chemistry (green chemistry and engineering) and greenhouse gas control, and
- Replacement of environmentally hazardous catalysts in existing processes.

5 Relevance of the research

Both Universities, the University of Oulu and Åbo Akademi University, have long traditions in education and research on heterogeneous catalysis, both in process and environmental catalysis. The former professors, Professor Väinö Veijola at Oulu University and Professor Lars-Eric Lindfors at Åbo Akademi, have created a solid basis for catalyst education and research and have offered their students a fruitful and rewarding environment to do research and become experts in the field of catalysis. Prof. Riitta Keiski at Oulu University and Academy Prof. Tapio Salmi at Åbo Akademi University have followed the steps of these two esteemed professors. The two Universities have mutual and separate interests in heterogeneous catalysis, i.e. the catalysis research group at Oulu University is mostly working to develop catalysts for pollution prevention, hydrogen and other biofuels production, and CO₂ utilization whereas the Åbo Akademi group is concentrating on the role of catalysts in fine chemicals production and design of catalytic processes. Both have a mutual interest towards sustainable production and energy, intensification of processes via the use of improved and nanostructured catalysts. Collaboration between these groups has been fruitful for years and has resulted in many high-level publications, M.Sc. and PhD theses.

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References

- Anastas, P. T. & Warner, J. C., Green Chemistry: Theory and Practice. New York 1998, Oxford University Press. p. 30.
- Anastas, P.T., Heine, G.L. & Williamson, T.C. (Editors). Green Engineering. Washington 2001, Oxford University Press. 252 p.

- Anastas, P.T. & Williamson, T.C., *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes*. Oxford 1998, Bookcraft Ltd. 364 p.
- Ballivet-Tkatchenko, D., Chambrey, S. Keiski, R., Ligabue, R., Plasseraud, L., Richard, P. Turunen, H. *Catal. Today* 115 (2006) p. 80.
- Brundtland report. World Commission on Environment and Development, Report of the World Commission on Environment and Development: Our Common Future. Transmitted to the General Assembly as an Annex to document A/42/427 - Development and International Co-operation: Environment. 1987, URL: <http://www.un-documents.net/wced-ocf.htm> (May 2, 2009)
- Centi, G., Ciambelli, P., Perathoner, S. & Russo, P. *Catal. Today* 75 (2002) p. 3.
- Centi, G. & Perathoner, S. *Catal. Today* 138 (2008) p. 69.
- Centi, G. & van Santen, R., *Catalysis for Renewables*. Weinheim 2007, Wiley-VCH Verlag GmbH & Co. KGaA. 448 p.
- Clark, J.H. *Green Chem.*, February (1999) p. 1.
- Ehfeld W., Hessel V. & Löwe H. *Microreactors*. Weinheim 2000, Wiley-VCH Verlag GmbH. 288 p.
- Grunes, J., Zhu, J. & Somorjai, G.A. *Chem. Comm.* (2003) p. 2257.
- Halmann, M.M. & Steinberg, M., *Greenhouse Gas Carbon Dioxide Mitigation*. Boca Raton 1999, Science and Technology, Lewis Publishers. 568 p.
- Jenssen, F.J.G. & van Santen, R.A. *Environmental Catalysis*. NIOK, *Catal.Sci. Series*, Vol. 1. 1999. 369 p.
- Kiwi-Minsker & Renken, *Catal. Today* 110 (2005) p. 2.
- Lowell Center for Sustainable Production. URL: <http://sustainableproduction.org/> (May 2, 2009)
- Pereira, C.J. *Chem. Eng. Sci.* 54 (1999) p. 1959.
- Somorjai G.A. *Nature* 430 (2004) p. 730.
- Richardson, J.T. *Principles of Catalyst Development*. New York 1989, Plenum Press. 288 p.
- Thomas, J.M. & Thomas, W.J. *Principles and Practice of Heterogeneous Catalysis*. Weinheim 1997, VCH. 669 p.
- Zhou, B., Hermans, S. & Somorjai, G.A. *Nanotechnology in Catalysis*, Vols 1-3. New York 2004, Springer. 555 p. & 333 p.

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