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# Catalysis in General Energy Research

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**Abstract.** For the storage of hydrogen in the form of synthetic liquid fuels, the reversible catalytic hydrogenation of toluene, and the catalytic hydrogenation of CO<sub>2</sub> yielding MeOH, are investigated. Catalytic processes are important in electrochemistry and, in particular, in the realization of electrodes with high power densities for low-temperature polymer electrolyte fuel cells. As a third area where catalysis is assigned a crucial role within General Energy Research, the treatment of exhaust gases from combustion processes will be discussed.

## 1. Introduction

The program of General Energy Research at PSI (Paul Scherrer Institute) includes the major aspects associated with society's energy needs, *i.e.* sources, storage, conversion, utilization, and ecological consequences. Energy is one of the key factors that will decide on sustainability: A dynamically growing world population with rapidly developing societies will have to undertake tremendous efforts for turning this development into one that is sustainable on a timescale beyond the year 2050.

With a view to sustainability, renewable energy sources are a first focal point of the program. With the exception of geothermal energy, renewable energies are based, either indirectly or directly, on

the flux of energy from the sun that is constant on a human timescale. Besides hydroelectric power, energetic utilization of biomass is an immediately available option, albeit of limited volume. At PSI we are investigating the gasification of waste biomass followed by MeOH synthesis from syngas. This is complemented by a long-term program in which energy carriers, such as hydrogen, are produced in a solar furnace by driving strongly endothermic reactions by means of concentrated sunlight [1].

There is an enormous need for intermediate storage of energy. As possibilities for direct storage of electric energy are important but limited, alternative options in terms of chemical energy storage are considered. Hydrogen will undoubtedly represent a major energy carrier of the future. However, for a variety of technical reasons there is a need for conversion of hydrogen into *liquid* secondary energy carriers. In this context, the reversible storage of hydrogen by hydrogenation of aromatic compounds, such as toluene, and by reduction of CO<sub>2</sub> yielding MeOH, are investigated at PSI.

Efficient energy conversion combined with reduction of specific process energy demand are the only measures that can counteract the expansion of global energy consumption caused by an increasing world population and rising *per capita* gross domestic product. Fuel cells are being developed at PSI both with a view to

efficiency and to local emission reduction. As these two criteria are crucial also for the long foreseeable time period in which fossil fuels will continue to be used, the investigation of low-NO<sub>x</sub>-efficient combustion processes represents another important research topic of the General Energy Research Department. Among the advanced combustion concepts pursued, catalytic combustion holds a large potential for reducing NO<sub>x</sub> emissions while, at the same time, maintaining high efficiencies.

Assessment of ecological consequences of energy use implies balancing life cycle emissions for various power generation options, experimental tracing of pollutants from emission *via* atmospheric transport to deposition, quantification of uptake by ecosystems, and estimation of damages caused in both natural and technical systems. Possible consequences of CO<sub>2</sub> emissions on climate change should be counteracted by economically realistic measures for CO<sub>2</sub> reduction. These questions are pursued in within a program for the Comprehensive Assessment of Energy Systems (Ganzheitliche Betrachtung von Energiesystemen, GaBE).

Catalysis is a key technology for many of the issues mentioned in the above brief survey. Catalytic research at PSI is focused on advancing innovative technologies in the areas of energy storage, conversion, and low emission energy use. Examples that will be discussed include the storage of hydrogen by catalytic hydrogenation, catalysts for low-temperature fuel cells, and exhaust-treatment catalysts for internal combustion engines.

## 2. Seasonal Energy Storage of Hydrogen

Seasonal mismatch is a well-known problem in hydroelectric power generation: Production peaks during early summer, whereas highest demand occurs during winter months. As the capacity limit of existing water pump storage reservoirs is approached, chemical storage is considered as an alternative to the mentioned conventional method. This alternative route, investigated by T.H. Schucan and E. Newson at PSI, starts with producing hydrogen using off-peak electricity during summer (Fig. 1). As the storage of compressed gaseous hydrogen becomes prohibitively expensive over periods exceed-

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ing one week [2], the hydrogen is converted into a liquid storage compound, methylcyclohexane, by toluene hydrogenation. Handling and storage of methylcyclohexane are comparable to the established gasoline storage technology. Upon demand, the hydrogen is recovered by catalytic dehydrogenation, and the toluene carrier is recycled. Electricity is then produced in, e.g., a molten carbonate fuel cell.

Overall efficiencies will depend on the use of heat released in the fuel cell for providing the enthalpy of the endothermic dehydrogenation reaction, and are predicted to vary between 25 and 38%. Whereas the energetic efficiency is much lower than the one of pump storage, the chemical storage of hydrogen may still be economically attractive, in view of the smaller investment required for setting up the chemical cycle, as compared to the high costs involved in constructing new, or expanding existing pump storage reservoirs in the Alps. Environmental concerns provide an additional incentive for investigating the chemical storage concept.

While hydrogenation of toluene is a facile exothermic process that may be accomplished with energetic efficiencies of 99%, the dehydrogenation reaction required considerably more attention. For a cyclic process, cracking of methylcyclohexane had to be avoided, and the amount of by-products decreased below 1%. Both goals have been achieved by modifying the reactivity of the noble-metal catalyst by a sulfiding procedure [2].

In order to increase the turnover of methylcyclohexane dehydrogenation per unit volume of catalyst, a dual reactor concept has been conceived and realized [3]. It aims at shifting the equilibrium composition towards the desired toluene product, by removing hydrogen from the reaction mixture. This is achieved by inserting, in between the two fixed bed reactor units, a membrane separator unit that extracts hydrogen by means of diffusion through a thin (70  $\mu\text{m}$ ) Pd/Ag foil. Using this setup, conversion beyond the value set by chemical equilibrium for a single pass has recently been achieved [3].

For economic success of the concept, catalyst stand time and, eventually, possibilities for catalyst regeneration are key issues. It has been demonstrated that the observed slow decline (over a period of several hundred hours) is due to deposition of coke on the metallic components of the catalyst, as well as on the support. Coke was successfully removed by controlled heating in oxygen/nitrogen mixtures, restoring the original activity several times on the same catalyst batch [3].

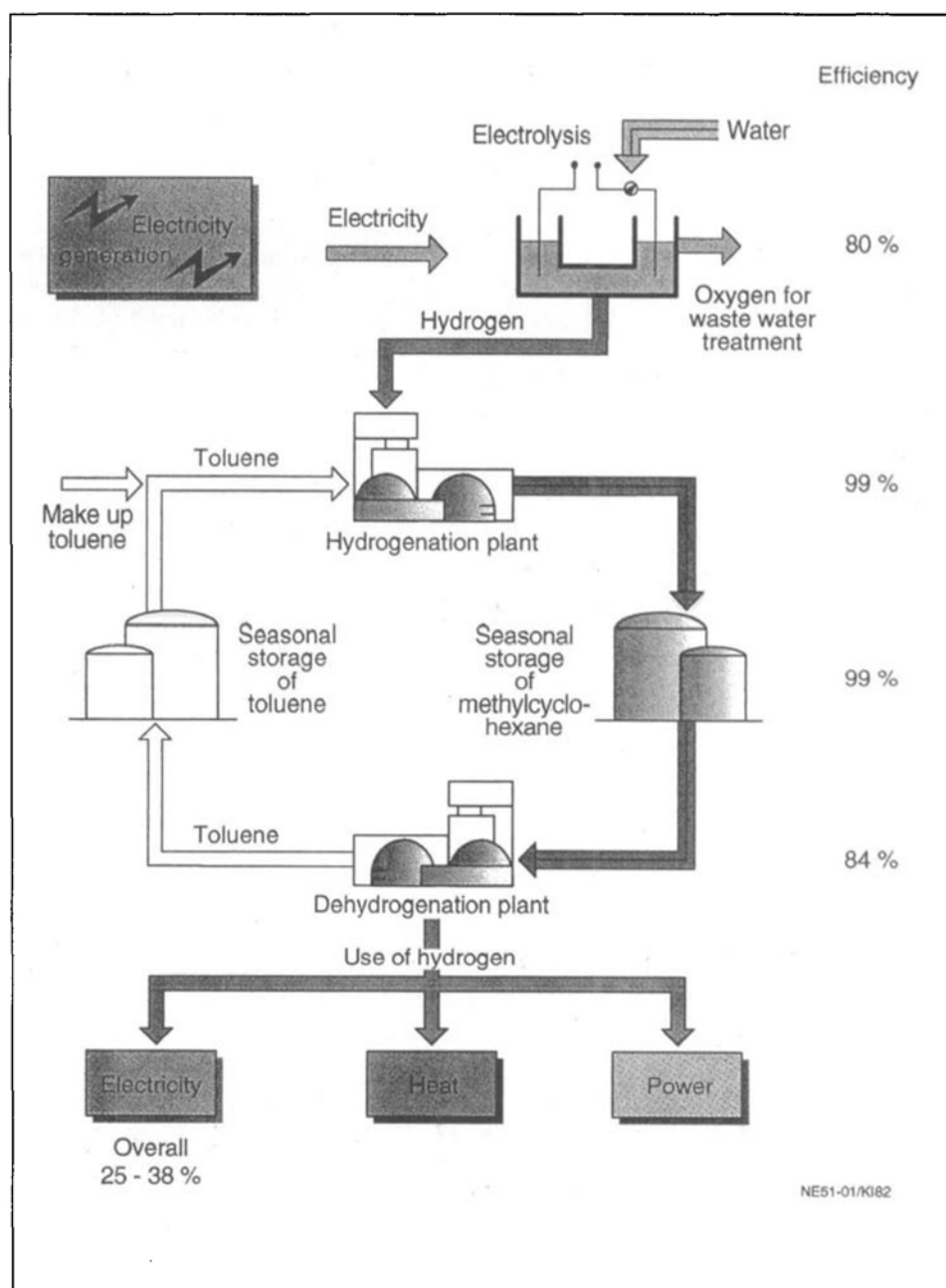


Fig. 1. Process scheme for the seasonal storage of hydrogen by toluene hydrogenation/methylcyclohexane dehydrogenation

### 3. Reversible Hydrogen Storage by Hydrogenation of $\text{CO}_2$ and MeOH-Steam Reforming

Synthesis of MeOH from  $\text{CO}_2$  and hydrogen has been proposed as an alternative route for storing hydrogen as a synthetic liquid fuel, and is compatible with the concept of a  $\text{CO}_2$ -neutral energy supply system. In collaboration with the group of A. Baiker, a series of *in situ* spectroscopic investigations has been performed aimed at elucidating the mechanism of MeOH synthesis over  $\text{Cu/ZrO}_2$  catalysts. It appears that the sequence of reaction steps occurring over  $\text{Cu/ZrO}_2$  is somewhat different from the one established for commercial catalysts for MeOH synthesis from syngas, such as  $\text{Cu/ZnO/Al}_2\text{O}_3$ . As

an example, a series of connectivities of surface species derived from static and dynamic diffuse reflectance FT-IR measurements [4] is shown in Fig. 2. *In situ* observations at different pressures varying between 3 and 25 bar were found informative for correlating the signals of the various surface species [5].

Information on the chemical composition and oxidation state of the catalyst surface after exposure to reaction conditions, surface segregation phenomena, and depth-dependent concentration profiles, is valuable and required for an interpretation of the dependence of catalyst activity on composition, activation procedures, and history of exposure to reactant gases. X-Ray photoelectron spectroscopy (XPS) is extensively employed to obtain this infor-

mation; depth profiles are recorded by ion sputtering of the surface, using XPS or secondary ion mass spectrometric (SIMS) detection. The results obtained may be exemplified by a recent study of surface-segregation phenomena that are occurring during reactive activation of amorphous metal alloys [6].

Complementing the efforts for developing active MeOH-synthesis catalysts, MeOH yield may be enhanced by innovative reactor design. A membrane reactor has recently been realized in which the

product, MeOH, is selectively removed from within the catalytic fixed bed reactor, using selectively permeable Nafion tube modules (Fig. 3). MeOH-Synthesis yield has been significantly enhanced in this design [7].

Complementing the storage of hydrogen by CO<sub>2</sub> hydrogenation, the release of hydrogen from simple alcohols is accomplished by steam reforming. Work at PSI has focused on sintering stability and coking resistance of steam-reforming catalysts. For the case of EtOH-steam reform-

ing, acetate has been identified as a key intermediate in the steam-reforming process [8].

#### 4. Catalysts for Low-Temperature Fuel Cells

Fuel-cell research at PSI focuses on the low-temperature polymer electrolyte fuel cell for mobile applications. Whereas high-temperature (molten carbonate and solid oxide) fuel cells are attractive for station-

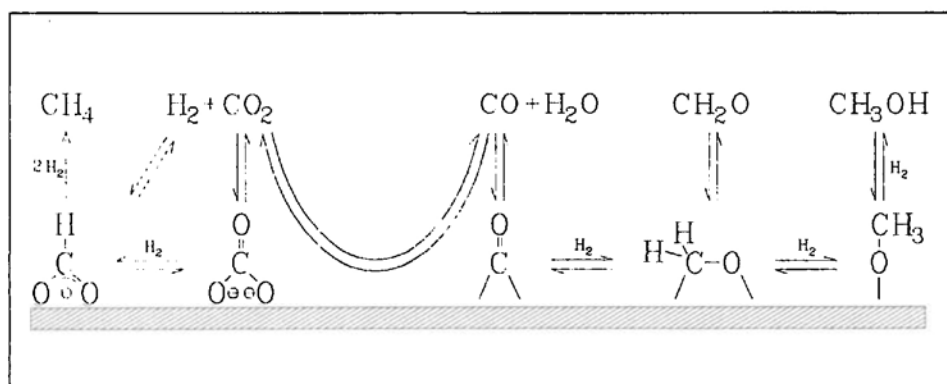


Fig. 2. Surface reactions involved in the catalytic synthesis of MeOH over Cu/ZrO<sub>2</sub> catalysts (for a detailed discussion, see [4])

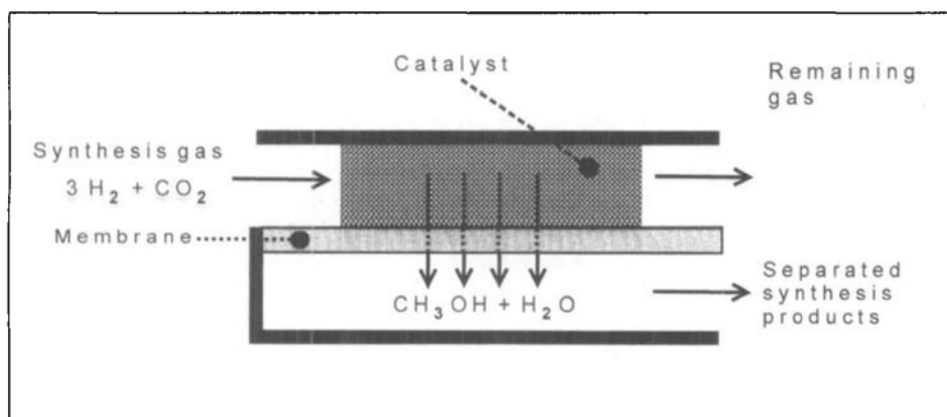


Fig. 3. Membrane reactor for MeOH synthesis. The yield is enhanced by selective removal of the product, MeOH.

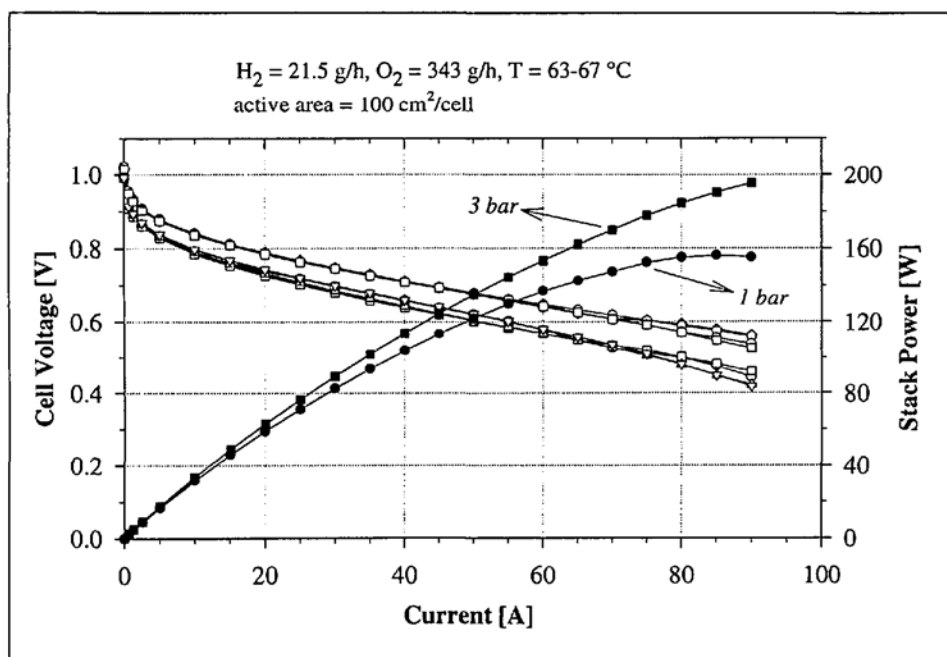


Fig. 4. Performance of the PSI low-temperature fuel cell. A bipolar stack consisting of four 100 cm<sup>2</sup> polymer electrolyte membrane cells was operated with hydrogen and oxygen at a pressure of 3 bar.

ary applications such as decentralized power stations where combined use of heat and electricity is feasible, there is general consensus that low-temperature cells (operating between 60° and 100°) are preferred for transport applications in buses, trucks, and, in particular, in passenger vehicles. They offer the advantages of cold start possibility, ease and safety of handling, potentially low weight, and adequate lifetime. Fuel cells are attractive for cars due to their intrinsically high efficiency which increases at partial load. This favorably contrasts the behavior of internal combustion engines which exhibit poorer efficiencies at partial load conditions under which they are operated most of the time.

In the polymer electrolyte fuel cell, hydrogen is passed over a Pt-coated carbon electrode, yielding protons and electrons that are transferred to the oxygen electrode via the external load where water is produced. The classical liquid electrolyte is replaced by a proton-conducting polymer membrane. Obviously, the current and power carried per unit area of this membrane are one of the factors that decide on overall performance. Work at PSI has focused on a novel proton-conducting polymer prepared by radiation grafting of styrene onto a fluorinated base polymer, followed by sulfonation [9][10].

Other factors that are crucial for fuel-cell performance are the flow and pressure of the reactant gases, hydrogen and air/oxygen, respectively, their distribution within the electrodes and the management of heat and water flows through the cell. These issues are tackled in the stack design project in which several elementary cells are combined into a bipolar stack. In 1995, the group of G. Scherer has succeeded in demonstrating 195 W of power in a stack consisting of four PSI membrane cells, of 100 cm<sup>2</sup> area each, using 3 bar of oxygen as the oxidant medium (Fig. 4) [11].

The 'bipolar plates' which separate the cells have to perform several functions, *i.e.* direct the flows of reactant gases and water, in addition to conducting the substantial current (1 A cm<sup>-2</sup>) and supporting the electrodes. Future development will, therefore, aim at producing thin bipolar plates from light-weight materials by using microstructuring techniques. It is here that a significant impact of catalytic research is envisaged, by incorporating the catalytic function on the surface of the bipolar plates.

The two specifications of a fuel cell of relevance to the car manufacturing industry are aggregate cost and aggregate weight per unit of power. Hence, the development

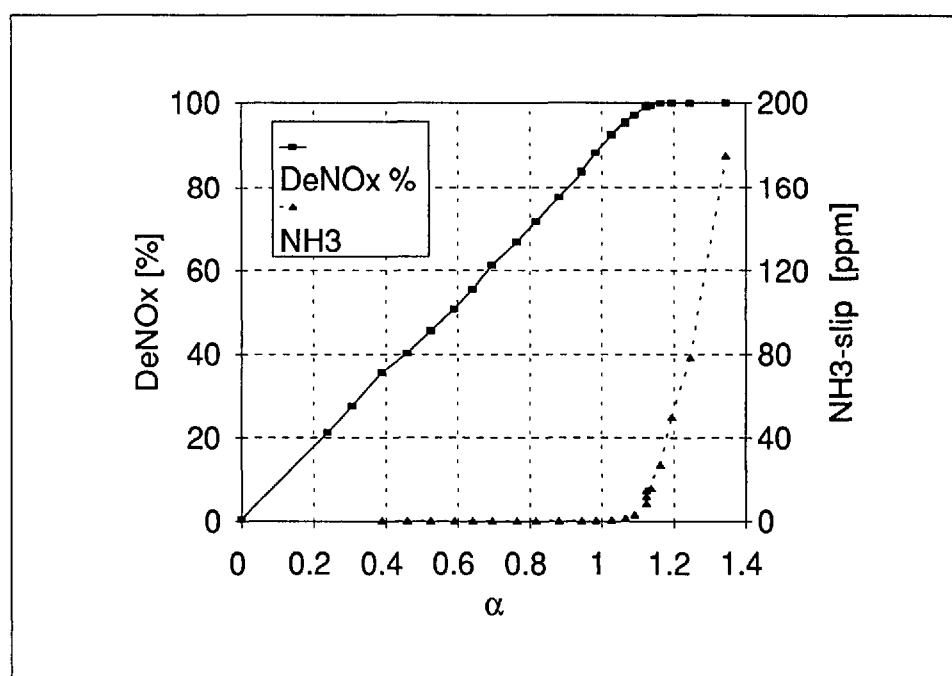


Fig. 5. Degree of NO<sub>x</sub> reduction and NH<sub>3</sub> slip as a function of the stoichiometry factor (see text). The Diesel generator was operated at 100 kW<sub>el</sub>; catalyst temperature was 455°.

of low-weight bipolar plates with efficient, moderately priced catalysts may decide on whether fuel cells will find their way into the passenger car market, *e.g.* as range extenders for fuel cell vehicles.

## 5. Exhaust-Gas Treatment

For the abatement of NO<sub>x</sub> in lean exhaust-gases containing excess oxygen, the selective catalytic reduction (SCR) of NO using NH<sub>3</sub> has been established as the most powerful catalytic technique, which is used worldwide in fossil-fuel power plants. Work of M. Koebel *et al.* at PSI has focused on the development of SCR for small decentralized applications, such as emergency Diesel generators or combined block heating/power stations, where the use of NH<sub>3</sub> is not viable in view of safety considerations. This reducing agent may, however, be conveniently generated by thermolysis or combined thermolysis/hydrolysis of an aqueous solution of the precursor molecule, urea.

The thermolysis and hydrolysis reactions of urea have been studied first, in order to verify the absence of undesired or even toxic side products resulting from urea decomposition. It was verified that after passage through the SCR catalyst at typical operating temperatures, no gaseous products other than those found in NH<sub>3</sub> SCR are present in the exhaust-gas stream. Recent experiments have investigated the possible conversion of urea into higher-molecular mass compounds, such as cyanuric acid or biuret; no appreciable

amounts were detected under typical operating conditions [12].

The design goal for a urea-SCR unit to be operated with a Diesel engine is, of course, complete conversion of NO in the exhaust-gas stream without the production of N<sub>2</sub>O or other undesired products. Not unexpectedly, the NO<sub>x</sub> conversion can be enhanced by increasing the dosing of the urea reducing agent, albeit at the expense of NH<sub>3</sub> slip. In view of the toxicity of NH<sub>3</sub>, the latter must by all means be avoided. Catalyst performance may thus be judged by plotting both NO conversion and NH<sub>3</sub> slip as a function of the stoichiometry factor, defined as the ratio of urea dosed to the quantity required from the stoichiometry of the reduction reaction. Such a plot (Fig. 5) shows that attractive NO removal has been achieved at PSI using a commercial V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> De-NO<sub>x</sub> catalyst [13].

These results suggest that use of an excess of urea would positively influence the NO<sub>x</sub> abatement, provided that excess NH<sub>3</sub> can be converted into nitrogen in a subsequent catalytic step. Hence, the development of a selective oxidation catalyst, which oxidizes NH<sub>3</sub> up to the stage of molecular nitrogen, is pursued in collaboration with the group of Prof. A. Baiker (ETH-Zürich).

The logical next step is the transfer of novel catalyst concepts, which showed the potential of exceeding the activity of commercial catalyst formulations on the laboratory scale, onto catalyst supports of the geometry and sizes as used in the Diesel test stand. Considerable materials devel-

opment is required for this purpose. In particular, sol-gel techniques will be applied for coating ceramic honeycomb structures with oxidic materials serving as catalyst supports.

A further project related to environmental catalysis is the study of catalytic CO oxidation at low temperatures. This reaction is known to exhibit a complicated dependence on CO partial pressure over Pd and Pt catalysts, including the possibility of oscillatory time dependence. Modulation techniques [14] have been proven valuable for visualizing the time-dependent behavior, and are holding promise for the elucidation of the CO-oxidation dynamics in multicomponent mixtures.

## 6. Outlook

The project for seasonal storage of hydrogen has reached a stage where steps relevant for the transfer to industry are being initiated. The schedule involves demonstration of the catalytic dehydrogenation of methylcyclohexane in a pilot plant at PSI designed for a toluene feed of 30 kg h<sup>-1</sup>. Successful operation of the pilot is a prerequisite for the construction of a demonstration plant which, with another scale-up by a factor of 10, is intended to realize the complete seasonal hydrogenation/dehydrogenation cycle. Experience with the latter plant is supposed to provide the facts necessary for a decision on a large scale (1000 GWh storage capacity) industrial implementation.

Examples mentioned in the preceding sections show not only that catalysis research at PSI is focused on the projects investigated in the context of sustainable energy technologies, but will inevitably occur at the interfaces with other disciplines. An obvious first interface is the development of catalytically active electrodes for use in fuel cells. Further attractive opportunities in electrochemistry are seen in the development of reversible oxygen electrodes for rechargeable metal/air batteries, such as Zn/air batteries, and in the synthesis of materials to be used as insertion electrodes in ion-transfer batteries. At PSI the group of S. Müller obtained encouraging results using La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub> perovskite as a bifunctional catalyst for the reversible oxygen electrode [15]. Highly dispersed metal oxides, e.g. obtained as xerogels [16] or by sol-gel techniques [16b], have been successfully tested as Li insertion materials.

Catalysis is crucial for the exhaust-gas treatment project. Transfer of novel catalysts that have shown excellent activities

and selectivities in laboratory testing, onto support structures such as honeycombs used in exhaust catalyst modules, will require significant efforts in coating technology and associated materials development. The design of selective oxidation catalysts, tailored for converting into nitrogen any excess NH<sub>3</sub> slipping from the DeNO<sub>x</sub> unit, is pursued in collaboration with ETH-Zürich.

A third interface, the importance of which is widely realized, is the intensive use of characterization techniques. Tools that will be employed include diffraction and electron-spectroscopic techniques, to yield information on bulk and surface structure and composition, respectively. Short-range order and local coordination, which are profoundly influencing the activity of amorphous or nanocrystalline materials, may be powerfully accessed by monitoring extended X-ray absorption fine structure (EXAFS), using synchrotron radiation. These studies are supplemented by the *in situ* monitoring of adsorbed species on catalyst surfaces, using optical techniques. Information obtained by the combined application of the mentioned methods provides the guidelines for the focused development of catalyst materials with improved performance and tailored properties.

Finally, catalyst development is intrinsically development of new materials, while on the other hand novel classes of materials (such as aerosols, aerogels, and oxidic coatings) have found important applications in heterogeneous catalysis. It is expected that interdisciplinary work on the borderline with materials science holds a high potential for advances in the field of energy catalysis.

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- [1] K. Ehrensberger, P. Kuhn, Proc. 10th World Hydrogen Energy Conference, Florida, 1994, p. 823; P. Kuhn, A. Steinfeld, A. Reller, Proc. 7th Symposium on Solar Thermal Concentrating Technologies, Moscow, 1994, p. 557; P. Kuhn, K. Ehrensberger, E. Steiner, A. Steinfeld, Proc. ASME/JSME/JSES International Solar Energy Conference, Hawaii, 1995, Vol. 1, p. 375.
- [2] S. Stucki, T.H. Schucan, in 'Global Link – Interkontinentaler Energieverbund', VDI-Berichte Nr. 1129, 1994, p. 175; E. Newson, T.H. Schucan, F. von Roth, T. Wyss, PSI Annual Report 1993, Annex V, 1994, p. 2.
- [3] A. Cuellar, Ph.D. Thesis, ETH-Zürich, 1996. A. Marin, E. Newson, P. Hottinger, J. Haueter, PSI Annual Report 1995, Annex V, 1996, p. 3.
- [4] C. Schild, A. Wokaun, A. Baiker, *J. Mol. Catal.* **1990**, *63*, 223; C. Schild, P.D. thesis, University of Bayreuth, 1991; J. Weigel, A. Wokaun, A. Baiker, *Fresenius J. Anal. Chem.* **1994**, *349*, 71.
- [5] J. Weigel, C. Fröhlich, A. Baiker, A. Wokaun, *Appl. Catal. A* **1996**, in press.
- [6] M. Kilo, G. Hund, A. Baiker, A. Wokaun, *J. Alloys and Compounds* **1996**, in press.
- [7] R. Struis, S. Stucki, M. Wiedorn, *J. Membrane Science* **1996**, in press (3/96).
- [8] J. Highfield, F. Geiger, E. Uenala, T.H. Schucan, Proc. 10th World Hydrogen Energy Conference, Florida, 1994, p. 1039.
- [9] B. Gupta, F.N. Büchi, G.G. Scherer, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1931.
- [10] B. Gupta, G.G. Scherer, *Chimia* **1994**, *48*, 127.
- [11] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, *J. Electrochem. Soc.* **1995**, *142*, 3044.
- [12] M. Koebel, M. Elsener, *J. Chromatogr. A* **1995**, *689*, 164.
- [13] M. Koebel, M. Elsener, T. Marti, Proc. 3rd Int. Conf. on Combustion Technologies for a Clean Environment, Lisbon, 1995.
- [14] J. Kritzenberger, A. Wokaun, 95. Hauptversammlung der Deutschen Bunsen-Gesellschaft, Jena, May 1996, Book of Abstracts.
- [15] S. Müller, F. Holzer, O. Haas, C. Schlatter, C. Comminellis, *Chimia* **1995**, *49*, 27; S. Müller, K. Striebel, O. Haas, *Electrochim. Acta, Special Issue on Electrocatalysis* **1994**, *39*, 1661.
- [16] P. Novak, W. Scheifele, F. Joho, O. Haas, *J. Electrochem. Soc.* **1995**, *142*, 2544; J.C. Panitz, A. Wokaun, *Sol-Gel Science* **1996**, in press.