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UNITED NATIONS INDUSTRIAL
DEVELOPMENT ORGANISATION

INTERNATIONAL CENTRE FOR
SCIENCE AND HIGH TECHNOLOGY

CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BUENOS AIRES

FINAL REPORT

Workshop on

"Catalytic Technologies for Sustainable Industrial Processes"

Buenos Aires, Argentina, 28-30 November 2001

UNIDO PROJECT TF/GLO/00/105
CONTRACT No. : 2001/310

OBJECTIVES

The main objectives of the workshop were:

- To survey the potential of developing novel catalytic materials for sustainable industrial processes
- To identify the current environmental problems of chemical industry with respect to application of catalytic processes
- To survey the available catalytic technologies for the valorisation of renewable resources
- To survey the state of art in Latin-American countries
- To evaluate the priorities in the field of the countries from the region and formulate possible cooperative projects

ORGANIZATION

The workshop was organized jointly by the International Center for Science and High Technology (ICS), United Nations Industrial Development Organization, and Chemical Engineering Department of the University of Buenos Aires, Argentina.

The local Organizing Committee consisted of:
Prof. Carlos Apesteguia (Co-Chairman, University of Litoral, Santa Fe)
Prof. Miguel Laborde (Co-Chairman, University of Buenos Aires)
Dr. Norma Amadeo (University of Buenos Aires)
Prof. Graciela Baronetti (University of Buenos Aires)
Jorge de Celis (University of Buenos Aires)
Beatriz Irigoyen (University of Buenos Aires)
Susana Larrondo (University of Buenos Aires)
Dr. Fernando Mariño (University of Buenos Aires)
Daniel Parisi (University of Buenos Aires)
Roberto Tejeda (University of Buenos Aires)

DATES AND VENUE

The workshop was held on 28-30 November 2001 in Buenos Aires, Argentina, in the facilities of the Chemical Engineering Department of the University of Buenos Aires (UBA).

FUNDING

The expenditure sanctioned by UNIDO for this project was USD 25,000. The amount received from UNIDO on 8th November 2001 was USD 20,000 to cover the expenses towards the items listed in the budget. The hosting country (Argentina) contributed USD 6,100 towards various items. The Organizing Committee had covered tickets for all international participants and Argentin participants living outside of Buenos Aires. The arrangements for meals, hotel, etc., with reasonable costs and quality were made. A summary of the final budget is given in Appendix 1.

SCIENTIFIC PROGRAM

9 lectures of 50 min from International Experts, 7 Country Reports of 30 min and 5 oral 30-min presentations from Latin-American and Argentin Experts were presented during the workshop. The detailed workshop program is given in Appendix 2.

The key topics covered during the workshop were:

- Catalysis for sustainable fine chemicals synthesis
- Environmentally benign technologies
- Development of solid acids for replacement of homogeneous acid-catalysed industrial processes
- Catalytic technologies for gaseous and liquid emissions control
- Novel catalytic processes for environmental protection
- Country reports (of Latin American countries) in the relevant field

PARTICIPATION

Several forms, invitation letters, and a printed Circular (which is included in Appendix 2) were disseminated among most of the academic institutions, R&D institutes and industrial companies in order to acquire attendance of several lecturers and participants from the following countries: Argentina, Peru, Bolivia, Ecuador, Brazil, Cuba, Chile, Colombia, Venezuela, Uruguay, Paraguay, Mexico, Belgium, Germany, USA, France, Spain, Italy, Canada, Netherlands. 69 participants and lecturers from 13 different countries including Argentina, Brazil, Chile, Colombia, Mexico, Uruguay, Venezuela, Netherlands, USA, Italy, France, Canada and Spain took part in this workshop. Participants' affiliations included universities (45.4 %), R&D centers (31.0 %) and industry (23.6 %). Distribution of the participants according to countries is shown in Table 1.

Table 1. Participants according to countries

No.	COUNTRY	NUMBER OF PARTICIPANTS
1	Argentina	35
2	Brazil	3
3	Chile	2
4	Mexico	1
5	Colombia	2
6	Venezuela	3
7	Uruguay	2

List of lecturers and speakers of oral presentations from different countries are given in Tables 2, 3, and 4. The complete lists of participants and lecturers are attached (Appendix 3).

Table 2. List of International Experts of the workshop

No.	Keynote Lecturer	Institution	Country
1	M. CLERICI	Eni Technologie , Milan	Italy
2	G. CENTI	University of Messina	Italy
3	P. FORNASIERO	University of Trieste, Trieste	Italy
4	P. GALLEZOT	Institut de Recherches sur la Catalyse, Lyon	France
5	D. LOFFLER	IDATECH, Oregon	USA
6	B. PEPPLEY	Royal Military College of Canada, Kingston, Ontario	Canada
7	J. PEREZ PARIENTE	Instituto de Catálisis y Petroleoquímica, Madrid	España
8	F. TRIFIRO	University of Bologna, Bologna	Italy
9	H. van BEKKUM	Delft University of Technology, Julianalaan	Netherlands

Table 3. List of Latinoamerican Experts of 30-min Country Reports

N°	**Speaker**	**Institution**	**Country**
1	C. APESTEGUIA	University of Litoral, Santa Fe	Argentina
2	J. BUSSI	University of La República, Montevideo	Uruguay
3	J. DOMINGUEZ	Mexican Institut of Petroleum, México D.F.	México
4	C. MONTES	University of Antioquia, Medellin	Colombia
5	J.L. MONTEIRO	COPPE/University of Rio de Janeiro	Brazil
6	G. PECCHI	University of Concepcion, Concepción	Chile
7	M.J. PEREZ ZURITA	Central University of Venezuela, Caracas	Venezuela

Table 4. List of Latinoamerican and Argentin Experts of 30-min oral presentations

N°	**Speaker**	**Institution**	**Country**
1	E. FALABELLA	CENPES / Petrobras, Río de Janeiro	Brazil
2	O. FERRETTI	University of La Plata, La Plata	Argentina
3	D. GOMEZ	National Committee of Atomic Energy, Buenos Aires	Argentina
4	M. LABORDE	University of Buenos Aires, Buenos Aires	Argentina
5	N. MARTINEZ	PDVSA Intevep, Caracas	Venezuela

WORKSHOP MATERIALS

Each participant and lecturer was provided with a workshop bag containing the following:

Abstracts of invited lecturers, oral and poster presentations
Handouts of the lectures and presentations
Detailed workshop program
List of participants with their mailing addresses
Pen and notebook
Identification badge
Tickets for coffee breaks and lunch

OPENING CEREMONY

The Opening Ceremony of the workshop was organized at the Conference Hall of Chemical Engineering Department of the University of Buenos Aires. The function was presided over by Professor C. Apesteguía, co-chairman of local organizing committee of the workshop.

SOCIAL EVENTS

Lunches and dinners were organized for all participants of the workshop. A welcome reception was given on the first evening of the workshop. A workshop dinner including a tango-show was organized on the second day for all participants in a typical restaurant of the historical San Telmo district.

RECOMMENDATIONS FOR FOLLOW-UP ACTIONS

In closing session, a plenary discussion based on Latin-American country reports was held. Main subjects of regional interest treated were: i) Use of bioethanol, ii) Future of biodiesel, iii) Carbohydrates as raw materials, iv) C_1 chemistry. The following conclusions were drawn:

- The use of ethanol as fuel for alcohol running motors, as it happened in Brazil years ago, failed because of economical and environmentally reasons. In contrast, the use of ethanol as raw material for petrochemical catalytic routes (alcochemistry), such as production of acetaldehyde, acetic acid, and ethylbenzene, is technically feasible and may help the economic development of rural areas in the region. It was also proposed to intensify studies on catalytic technologies for treating residues originated in the fermentation, since ethanol production involves the generation of a very pollutant residue.

- Because of capacity reasons it was considered that biodiesel could never totally replace diesel. But biodiesel could replace part of the metropolitan diesel (very low sulfur levels) in some very polluted areas. Production of biodiesel in Latin-American countries that are big producers of soybean oil, such as Argentina or Brazil, may be important for regional economies. In general, oil chemistry is considered of great potential for the region and the development of new catalytic routes to explore the potential of molecules existing in vegetable oils should be stimulated.

- Use of carbohydrates as raw materials for producing pharmaceuticals, fragrances, and other fine chemicals appears of particular regional interest. Catalytic routes in sucrochemistry are well established and work very well. In contrast, the use of carbohydrates as raw materials for fuels is limited for the same problems concerning bioethanol or biodiesel.

- Production of natural gas is rapidly expanding in several Latin-American countries, namely Argentina, Colombia, Venezuela, Mexico, and Brazil. There is a need of new catalytic technologies for obtaining valuables chemicals from natural gas. It was considered especially important for the region the Gas to Liquid processes for generation of: i) sulfur free diesel; ii) high quality paraffins for petrochemistry; and (iii) alkanes to replace olefins. Also, the use of natural gas as raw material for petrochemicals, such as dimethyl ether (DME), olefins and halogenated derivatives.

- The local organizing committee will contact the editors of Latinamerican Applied Research Journal (international journal edited in Argentina) in order to publish in a special issue the manuscripts derived from the lectures presented in this workshop. It was also recommended to ICS-UNIDO to evaluate the possibility of publishing selected papers presented during the workshop in a special issue of the Italian scientific journal "La Chimica e l'Industria" (as a joint publication with ICS-UNIDO).

- The organization of this type of events was considered of great importance for Latin America and, in general, for developing countries, and a common will was expressed for the continuation of the UNIDO support. In particular, it was recommended as a priority the organization a Regional School of postgraduates in the field of catalytic technologies for sustainable development.

CLOSING CEREMONY

Prof. C.R. Apesteguía and Dr. M.G. Clerici expressed their satisfaction of the high scientific quality of presentations and activity of all participants.

APPENDIXES:

Appendix 1:
Budget Table

Appendix2
Circular and Program of the workshop

Appendix 3
List of lecturers and participants

Appendix 4
Book of Abstracts

UNITED NATIONS INDUSTRIAL
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INTERNATIONAL CENTRE FOR
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CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BUENOS AIRES

FINAL REPORT: Appendix 1

Workshop on

"Catalytic Technologies for Sustainable Industrial Processes"

Buenos Aires, Argentina, 28-30 November 2001

UNIDO PROJECT TF/GLO/00/105
CONTRACT No. : 2001/310

Catalytic Technologies for Sustainable Industrial Processes
Buenos Aires, Argentina, 28-30 November 2001
Catalysis (1.1)

Rate of Exchange: 1 /dollar

BUDGET UNIDO

TOTAL FUNDS FROM ICS-UNIDO

DESCRIPTION	Budget in US$	Budget local curr.	Disbursement US	Disbursement l.c.	Difference USD$	Difference l.c.
Travels						
International lecturers	8,400	8,400	9,114	9,114	-714	-714
Gabriele Centi			930	930		
Paolo Fornasiero			1,035	1,035		
Pierre Gallezot			1,701	1,701		
Daniel Löffler			1,150	1,150		
Ferruccio Trifiro			1,090	1,090		
Brant Peppley			1,145	1,145		
J. Perez Pariente			1,177	1,177		
Herrman van Bekkum			886	886		
Latinoamerican lecturers	6,400	6,400	4695	4695	1705	1705
Juan Bussi			121	121		
José M. Dominguez			965	965		
Eduardo Falabella			502	502		
Nelson Martinez			582	582		
Consuelo Montes			818	818		
José L. Monteiro			502	502		
Gina Pechi			479	479		
María J. Perez Zurita			582	582		
Carlos Apesteguia			144	144		
Total travels	**14,800**	14,800	13,809	13,809	991	991
Accomodation & meals						
international lecturers and participants	**6,300**	6,300	6,900	6,900	-600	-600
national lecturers and participants	**2,900**	2,900	3,160	3,160	-260	-260
Total accomodation	9,200	9,200	10,060	10,060	-860	-860
Local Transport	**650**	650	710	710	-60	-60
Publication of Proceedings	**350**	350	380	380	-30	-30
GRAND TOTAL	**25,000**	25,000	24,959	24,959	**41**	**41**

TOTAL BUDGET FROM UNIDO	**25,000**
ALREADY TRANSFERRED AMOUNT (80%)	**20,000**
REMAINING FUNDS TO BE TRANSFERRED (after actual disbursement)	**4,959**

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY

CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BUENOS AIRES

FINAL REPORT: Appendix 2

Workshop on

"Catalytic Technologies for Sustainable Industrial Processes"

Buenos Aires, Argentina, 28-30 November 2001

UNIDO PROJECT TF/GLO/00/105
CONTRACT No. : 2001/310

ROFILE OF PARTICIPANTS

workshop is intended for participants from R&D tutes, industries and universities working in catalysis and ess development for sustainable chemical synthesis and ntamination.

resentatives of Latin-American countries and rnational experts are invited as lecturers.

TENTATIVE PROGRAMME

following main topics will be covered during the kshop:

atalysis for sustainable fine chemicals synthesis
nvironmentally benign technologies
evelopment of solid acids for replacement of omogeneous acid-catalysed industrial processes
atalytic technologies for gaseous and liquid emissions ontrol
ovel catalytic processes for environmental protection
ountry reports (of Latin American countries) in the elevant field

official language of the workshop is English.
l program will be sent for participants after reception of registration form.

CCOMODATION AND SOCIAL PROGRAMME

invited participants and lecturers supported by ICS to rticipate in the workshop, roundtrip air ticket will be ovided for the most direct and economical route. The ganizers in consultation with the participants will issue the epaid tickets.
vited participants will be accommodated in a hotel in enos Aires during the meeting (full board for 4 days).

REGISTRATION FORM

Registration and participation in the workshop are free

Name

Surname

Institution

Address

E-mail

Fax

Phone

Please complete and return by fax or e-mail to
Dr. Carlos Apesteguia

SITE

The workshop will be held in Buenos Aires in the facilities of the Chemical Engineering Department of the University of Buenos Aires (UBA). UBA is the biggest university in Argentina and has a strong current position in the fields of question of this workshop.

In Argentina, a considerable research potential in catalysis has been formed. In the academy, there are several active research groups working in the field of catalysis at INCAPE and INTEC (University of Litoral, Santa Fe), CINDECA (University of La Plata), INTEQUI (University of San Luis), INIQUI (University of Salta), PLAPIQUI (University of Bahia Blanca), INTEMA (University of Mar del Plata), CITeQ (Technological University of Cordoba), Department of Chemical Engineering of the University of Buenos Aires. The basic research is directed to a wide range of problems of essential importance for the development of the catalytic science. Intensive applied studies are also being carried out.

ORGANIZING COMMITTEE

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Dr. Miguel Laborde (FIUBA-Conicet, Co chair)
Dra. Norma Amadeo (FIUBA-Conicet)
Ing. Graciela Baronetti (FIUBA-Conicet)
Ing. Jorge de Celis (FIUBA)
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TERNATIONAL CENTER FOR SCIENCE AND HIGH
TECHNOLOGY OF THE UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

Workshop on

Catalytic Technologies for Sustainable Industrial Processes

Buenos Aires, Argentina
28-30 November 2001

Organized by the
International Center for Science and High
Technology (ICS-UNIDO) in cooperation with
Chemical Engineering Department of
University of Buenos Aires

AIMS AND SCOPE OF THE WORKSHOP

The industrial and social interest of the countries in trans and developing countries from Latin America is to eval the place and role of catalysis in the correspon contemporary economies, essentially in the improveme the industrial catalytic processes and in the abateme contamination. Industrial development may not conceived without sustainable chemistry. In tur technology is sustainable as along as it meets the nee the present without compromising the ability of fu generations to meet their needs. Industrial develop therefore requires proper planning not only for technolo success but also to allow future generations to meet t needs. The adoption of environmentally benign cata technologies in chemical designs is a key issue for achievement of their economic and environmental goals.

The main objectives of the workshop are:

- To survey the potential of developing novel catalytic materials for sustainable industrial processes
- To identify the current environmental problems of chemical industry with respect to application of catalytic processes
- To survey the available catalytic technologies for the valorisation of renewable resources
- To survey the state of art in Latin-American countries
- To evaluate the priorities in the field of the countries from the region and formulate possible cooperative projects

The expected outputs of the workshop are:

- Survey of catalytic technologies for sustainable industrial processes
- Survey of current situation in Latin-American countries
- Transfer of information and knowledge in advanced areas of catalysis and clean technologies from experts from R&D institutes, industries and universities
- Proposals for follow-up projects focusing on sustainable catalytic technologies.

Workshop on

Catalytic Technologies for Sustainable Industrial Processes

Buenos Aires, Argentina

28-30 November 2001

Organized by the
International Centre for Science and High Technology (ICS-UNIDO)
in cooperation with Chemical Engineering Department of
University of Buenos Aires

Program

Wedsnesday, 28 November 2001

9:00-9:30 Registration

9:30-9:45 **Opening Ceremony**

Introductory Session

9:45-10:10 ICS-UNIDO Programmes and Activities in the Area of Chemistry, with special focus on the subprogramme of Catalysis *(M. Clerici, ICS-UNIDO)*
Chairman address *(C. Apesteguía, Co-chair)*

10:10-10:30 *Coffe Break*

Session one

Sustainable Catalytic Technologies I
Session chair: J.M. Dominguez

10:30-11:20 Renewable materials and their increasing role as chemical feedstock
(*H. van Bekkum, The Netherlands*)

11:20-12:10 Design of new heterogeneous catalysts for the synthesis of biodegradable surfactants from renewable resources
(J. Perez Pariente, Spain)

12:10-12:30 Discussion

12:30-14:00 *Lunch Break*

Session two

Country Reports
Session chair: G. Centi

14:00-14:30 Country Report: Argentina
(C. Apesteguía, Argentina)

14:30-15:00 Country Report: Chile
(G. Pecchi, Chile)

15:00-15:30 Country Report: Venezuela
(J. Perez Zurita, Venezuela)

15:30-16:00 Discussion

16:00-16:30 *Coffe Break*

Session three

Processors for Fuel Cell Power Generation
Session chair: M.J. Perez Zurita

16:30-17:20 Fuel processors for fuel cell power generation
(D. Löffler, USA)

17:20-18:10 Methanol Fuel Processing for Fuel Cell Power Systems: Catalysis, Kinetics and System Optimization
(B. Peppley, Canada)

18:10-18:30 Discussion

Thursday, 29 November 2001

Session four

Environmentally Benign Technologies I
Session Chair: C. Montes

9:00-9:50 Oxidation Heterogeneous Catalysis for Clean Processes
(F. Trifirò, Italy)

9:50-10:00 Discussion

10:00-10:30 *Coffe Break*

Session five

Country Reports
Session Chair: B. Peppley

10:30-11:00 Country Report: Brazil
(J.L. Monteiro, Brazil)

11:00-11:30 Country Report: Colombia
(C. Montes, Colombia)

11:30-12:00 Country Report: Uruguay
(J. Bussi, Uruguay)

12:00-12:30 Discussion

12:30-14:00 *Lunch Break*

Session six

Catalytic Technologies for Water and Air Depollution
Session Chair: G. Pecchi

14:00-14:50	Catalytic Technologies for Water Depollution *(G. Centi, Italy)*
14:50-15:40	Catalytic technologies for prevention/control of air pollution from mobile sources *(P. Fornasiero, Italy)*
15:40-16:00	Discussion
16:00-16:30	*Coffe Break*

Session seven

Clean Catalytic Technologies in Latinoamerican Oil and Petrochemistry Companies
Session Chair: P. Gallezot

16:30-17:00	Country Report: México Comparative study on the actual trends of R&D projects and market needs in the refining industry of Mexico *(J.M. Dominguez, IMP, México)*
17:00-17:30	Catalytic Technologies for Sustainable Industrial Processes: The role of PDVSA-INTEVEP *(N. Martínez, INTEVEP, Venezuela)*
17:30-18:00	Catalytic Technologies for Sustainable Industrial Processes: The role of Petrobras *(E. Falabella, Petrobrás, Brazil)*
18.00-18:30	Discussion

Friday, 30 November 2001

Session eight

Sustainable Catalytic Technologies II
Session Chair: J.L. Monteiro

9:00-9:50	Catalytic technologies for the conversion of renewables. Conversion of carbohydrates into fine chemicals (*P. Gallezot, France*)
9:50-10:10	Production of hydrogen and oxygenates from bioethanol *(M. Laborde, Argentina)*

10:10-10:30 Discussion

10:30-11:00 *Coffe Break*

Session nine

Environmentally Benign Technologies II
Session Chair: P. Fornasiero

11:00-11:50 Acid and redox zeolites in fine chemicals synthesis
(*M.Clerici, Italy*)

11:50-12:10 Partial oxidation and mixed reforming processes for syngas obtention
(O. Ferretti, Argentina)

12:10-12:30 The impact of the liberalisation of the electricity market on its enviromental performance for selected countries of Latinoamerica and Europe
(D. Gomez, Argentina)

12:30-13:00 Discussion

13:00-14:30 *Lunch Break*

Closing Session

14:30-15:30 Plenary discussion and presentation of recommendations for follow-up action

15:30-16:30 Recommendations and Conclusions

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CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BUENOS AIRES

FINAL REPORT: Appendix 3

Workshop on

"Catalytic Technologies for Sustainable Industrial Processes"

Buenos Aires, Argentina, 28-30 November 2001

Workshop on
Catalytic Technologies for Sustainable Industrial Processes
Buenos Aires, Argentina, 28-30 November 2001

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Workshop on

Catalytic Technologies for Sustainable Industrial Processes

Buenos Aires, Argentina, 28-30 November 2001

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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY

CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BUENOS AIRES

FINAL REPORT: Appendix 4

Workshop on

"Catalytic Technologies for Sustainable Industrial Processes"

Buenos Aires, Argentina, 28-30 November 2001

UNIDO PROJECT TF/GLO/00/105
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Workshop on

Catalytic Technologies for Sustainable Industrial Processes

Buenos Aires, Argentina

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Organized by the
International Centre for Science and High Technology (ICS-UNIDO)
in cooperation with Chemical Engineering Department of
University of Buenos Aires

Book of Abstracts

INTRODUCTION TO ICS-UNIDO PROGRAMMES

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The United Nations Industrial Development Organization (UNIDO) is a specialized agency of the United Nations dedicated to promoting sustainable industrial development in developing and transition-economy countries. It harnesses the joint forces of government and private sector to foster competitive industrial production and international industrial partnership and promote socially equitable and environmentally friendly industrial development.

The International Centre for Science and High Technology (ICS) is an institution within the legal framework of UNIDO, with headquarters located in Trieste, Italy at the AREA Science Park.

The Centre's mandate is the transfer of know-how and technology in favour of developing countries and is based on the premise that competitive industrial technological capability cannot be built-up without adequate scientific knowledge and commitment to a sustainable development approach based on new and environmentally friendly technologies.

One of the specific sectors within the present Work Programme the ICS's activities is Pure and Applied Chemistry. Priority fields in its work are key relevance to economic and industrial development and environmental protection. Among the is a subprogramme on Catalysis and Sustainable Chemistry.

ICS-UNIDO is promoting this programme focused on sustainable chemistry, catalysis and clean technologies. An important part of this programme is focused on the promotion of new technologies, which can be helpful for the reduction of pollutants in industrial processes and technologies for the elimination of PTS. Another issue is to promote the use of renewable resources in fine chemical production in developing and in transition countries.

This important scientific and technological area for the development of environmentally friendly chemical processes forms the basis for cleaner industrial development and are also the key element for an industrial pollution prevention approach. New, less pollutant processes together with the optimization of existing processes depend to a great extent upon the environment of catalyst performance in the heavy and fine chemical production lines with a direct impact on the generated by-products or waste. Another approach is to promote innovation by supporting the diffusion of clean technologies in small-medium enterprises and the use of renewable resources.

Pollution by chemical manufacturing can result from different causes: hazardous reagent and by-products, waste production, slowly degradable materials, inefficient processes. The recourse to catalytic methods and the use of renewable raw materials are two effective routes to reduce the impact of chemical processing on the environment.

Catalysis is a powerful tool in promoting the reduction of pollution and sustainable chemistry, through efficient atom incorporation in the products and the development of synthetic methods based on clean reagents. The oxidants, such as molecular oxygen and hydrogen peroxide, reducing agents such as hydrogen and solid acid catalysts are inherently safe and free on undesirable wastes. Catalysis can also promote a larger use of renewable raw materials for chemical and fuel production.

Crop-derived feedstocks are more sustainable, in the long term, than oil based ones. They are generally non-toxic and are biodegradable. It may be necessary, however, to reduce the transformation costs for they to become competitive with the traditional production routes. Environmental considerations, as well , might be of relevance in their use in manufacturing processes.

The concept of pollution reduction and prevention is especially important in the field of persistent toxic substances (PTS) pollution, where also several UN Agencies (e.g., UNEP and UN ECE) have been developing a series of actions focused on POPs and PTS issues.

RENEWABLE MATERIALS AND THEIR INCREASING ROLE AS CHEMICAL FEEDSTOCK

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The development of sustainable routes to chemicals and organic-chemical materials has been neglected since the discovery of plentiful oil supplies.

However, with an increasing population, up to 9 billion, and oil as well as gas stocks being finite, we should reconsider sustainable raw materials.

A scenario has been developed [1] including a plant-based chemical industry which could meet the needs of the planet's population in the middle of this century.

Biomass may be utilized in various ways:

(i) nature already produces the desired structures and isolation requires only physical methods;
(ii) in one or several chemo- or bio-catalytic steps organic chemicals and organic materials are obtained from natural products;
(iii) back to Bio synthesis gas or Biocrude

More and more total crop use is coming to the fore, in which methods (i)-(iii) are undertaken in concert, and co-production of bulk and fine chemicals takes place.

The lecture will review the growing chemical networks of major natural organic classes and of some nature-derived key molecules:

- carbohydrates [2], with the newcomer inulin,
- triglycerides [3],
- terpenes,
- the key molecules ethanol, methanol, lactic acid and succinic acid.

Moreover, for several chemicals oil-based and renewable-based synthesis routes will be compared. A recent example of fossil/green competition is the polyester monomer 1,3-propanediol. Chemo- and biocatalytic methods are indispensable and keep developing to higher selectivities [4].

A positive development is that two giant-companies, Dow Chemical (petrochemicals) and Cargill (renewables), have decided [5] to join forces in the large scale manufacture of starch- or sucrose-based poly-L-lactate. For recent articles on polylactate and starch-based biodegradable packaging materials, see ref. [6].

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DESIGN OF NEW HETEROGENEOUS CATALYSTS FOR THE SYNTHESIS OF BIODEGRADABLE SURFACTANTS FROM RENEWABLE RESOURCES

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The use of feedstock for the chemical industry proceeding from renewable resources is experiencing an increasing attention due to environmental constraints. Indeed, the full life cycle of chemical products should commit to severe regulations to decrease to acceptable levels their impact on the environment. This trend stimulates not only the use of products with high biodegradability, but also favors clean chemical processes who would progressively replace those developed under less severe environmental concerns.

In addition to these factors, efforts are made to reduce the energy input needed for the production of chemicals.

The surfactants constitute a strategic class of products due to their wide use in many chemical industries. As with many others chemicals, their nature and synthesis processes are also affected by environmental constraints.

The fatty acid monoesters of polyols, such as those of glycerol and sorbitol, are valuable surfactants having excellent biodegradability which are widely used as emulsifiers in the food, pharmaceutical and cosmetic industries, as well as polymers additives and lubricants. The industrial synthesis of these esters is carried out by two different procedures: direct esterification of polyol with a fatty acid, catalysed by homogeneous acid catalysts, such as sulfuric and sulfonic acids, or by transesterification of triglycerides and polyols catalysed by alkaline hydroxides. These procedures generate waste chemicals and lead to impure products. Beside, the yield to monoester is low, and the whole process required a high-energy consumption.

In this talk the development of heterogeneous acid catalysts for the selective and efficient esterification of glycerol with fatty acids ($C_{12} - C_{18}$) is presented. These catalysts are based on mesoporous materials containing organic sulfonic acid groups as active centers. The influence of different organic groups and operation conditions on the catalyst performance is discussed.

COUNTRY REPORT: ARGENTINA
CATALYTIC TECHNOLOGIES FOR SUSTAINABLE AND ENVIRONMENTALLY BENIGN PROCESSES IN ARGENTINA

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A short overview of the main research lines and projects in Argentina on catalytic technologies for sustainable chemistry, environmentally benign processes and gaseous and liquid emissions control is presented.

Projects on cataltysis for sustainable chemistry involve the production of hydrogen and oxygenates from bioethanol, fuels from waste polyethylene, selective catalytic hydrogenation for carbon dioxide recycling, fine chemicals synthesis via selective oxidation of terpenes and the production of acetal from ethanol and acetaldehyde

Projects on gaseous emissions abatement from mobile sources include the development of novel catalysts for diesel soot combustion and for the selective reduction of NO_x pollutants. Studies on the reformulation of gasoline involve the improvement of solid acid catalysts for efficiently producing octane number enhancers (alkylate, light paraffins) with fewer environmental objections. Research on the catalytic abatement of VOCs and HVOCs from stationary sources is focused in developing new highly active Pt-based catalysts for hydrocarbon combustion, and new alternative formulations, such as exchanged zeolites, for the complete oxidation of trichloroethylene

Main projects centered on the use of catalytic technologies for liquid emissions control include: i) Catalytic wet oxidation technology for waste water treatment (phenol oxidation on Cu-based catalysts); ii) Development of an intensified version of Fenton's process for refractory organic wastewaters and, iii) Study of the comparative efficiency of slurry and fluidized bed photocatalytic reactors for water pollutants abatement.

In the area of Environmentally Benign Technologies, projects include the development of new catalysts for the high-temperature combustion of methane, the replacement of liquid acids for solid acid catalysts in chemical synthesis and Fine Chemistry and the use of basic zeolites for side-chain alkylations.

COUNTRY REPORT: CHILE
CHILE REPORT IN THE RELEVANT FIELD

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1.- Photocatalysis

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Advanced Oxidation Processes in environmental applications

The homogeneous systems O_3/OH^-, H_2O_2/O_3, O_3/UV and H_2O_2/UV have been studied on chlorinated phenols and cellulose bleaching effluents. The photocatalytic systems TiO_2/UV, ZnO/UV and TiO_2/O_3/UV study in the degradation of celulose and textile effluents.

Jorge Villaseñor[1], Patricio Reyes[2], Gina Pecchi[2]. [1]:University of Talca, Talca. [2]:University of Concepción, Concepción.

Photocatalytic degradation of organic compounds

The ozonation photocatalitic activity on sol-gel and impregnated supported catalyst in the degradation of phenol and chlorophenol is studied. The study systems are Fe_2O_3/TiO_2, MnO_2/TiO_2, Fe_2O_3/Al_2O_3 and MnO_2/Al_2O_3.

2.- Reduction of NO

Paulo Araya, Jaime Retuert, Joaquín Cortés. University of Chile, Santiago.

Catalytic reduction of NO.

Rh and Rh-Pd/SiO_2 supported catalysts are studied to get relations between the catalytic activity, measured by DRIFTs, with the metal particle size.

Catalytic reduction of NO with CH_4 on noble metal oxide supported catalysts.

In sol-gel Pd/ZrO_2 and other systems supported catalysts is study the activity and resistance to sintering of these new catalysts. Additionally, the Monte Carlo theoretical simulation is studied.

3.- CWAO Process

Rafael García, Gabriela Soto, Renán Arriagada. University of Concepción, Concepción.

Catalytic wet air oxidation of ammonia and aliphatic amines.

Pt, Pd and Ru supported catalysts on activated carbons obtained from lignocellulosic materials (peach stone) are used in the CWAO of ammonia aliphatics amines. The surface oxygenated functional groups of the support are modified in order to study this effect on the activity and selectivity of the reaction.

4.- Catalytic combustion of VOCs

Patricio Reyes, Gina Pecchi. University of Concepción, Concepción.

Catalytic combustion of volatile organic compounds and mixtures on sol-gel and impregnated catalysts.

The activity, selectivity, thermal stability and resistance to deactivation in the reaction of combustion of methane and toluene of noble metals (Pt, Rh Pd) and oxides (Fe_2O_3, ZrO_2) supported on SiO_2 and TiO_2 catalysts prepared by impregnation and the sol-gel methods are studied. Additionally, the kinetic of the reaction in the Fe_2O_3/TiO_2 system is studied.

5.- Fine chemical

Patricio Reyes, Gina Pecchi. University of Concepción, Concepción

Selective hydrogenation and assymetric catalytic reactions

The activity and selectivity of different metal noble supported catalysts modified by the addition of promotors are studied in selective hydrogenation of α,βunsaturated aldehydes such us crotonaldehyde, cinnamaldehyde and citral. Additionally, hydrogenation of assymetric diones to the corresponding dioles are also studied.

COUNTRY REPORT: VENEZUELA

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Catalysis studies in Venezuela started in 1964 at the Science Faculty of the Universidad Central de Venezuela under the direction of Professor H. Noller from the Research Institute of Catalysis of Munich, Germany. This pioneer effort, gave rise to all existing catalysis groups in the country and to the Venezuelan Catalysis Society founded in 1983. Academia contribution to the open literature obtained from a search in Chemical Abstracts (1967 – present) using Venezuela and cataly* as keywords, gave a result of 251 papers, from which more than 100 correspond to the last 8 years. This result did not include some topics, such as homogeneous or theoretical works, surface chemistry, adsorption, etc., which are certainly indexed by different keywords. Obviously then, a sustained effort in research is permanently pursuit by the Venezuelan catalytic community. The presence of Venezuela in the Council of the International Congress was a reality last year.

Within the academia, various groups in universities (Universidad Central de Venezuela, Universidad de los Andes, Universidad de Carabobo, Universidad del Zulia and Universidad de Oriente), polytechnic institutes (Instituto Universitario de Tecnología: Región Capital and Cumaná) and research centres (IVIC) are devoted to different kind of studies mainly oriented towards two alternatives, one dealing with improvements on existing catalysts, and the other towards the development and applications of new materials. Among the main areas of research can be cited C1 chemistry, upgrading of heavy oil fractions, hydro treatment reactions, electronic and crystalline properties of transition metal sulphides, zeolite and molecular sieve catalysts, light alkanes transformations (aromatisation, hydrocracking, hydroisomerization, etc.) and bifunctional catalysis (kinetics, mechanism, deactivation), environmental catalysis, fine chemistry, pillared clays, characterization of metal and oxide catalysts, activated carbon and polymerisation process simulation.

International collaboration currently take place with France, Spain, Cuba, Great Britain, Chile, Italy, Mexico, USA and Hungary. While at the beginning, it was focused in human resources formation, it evolves, later on, towards research and development of joint projects.

FUEL PROCESSORS FOR FUEL CELL POWER GENERATION

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Because of their apparent simplicity and potential high fuel efficiency, fuel cells are being considered for providing power to vehicles, residences, and larger consumers such as hotels, hospitals, and small industrial plants. This renewed interest on fuel cells can be traced to the development, over the past decade, of affordable, lightweight electrodes and membranes that operate at low temperatures. Those materials made possible the polymer electrolyte membrane (PEM) fuel cell.

At present, commercially viable PEM fuel cells utilize only hydrogen fuel. Given the lack of an infrastructure for hydrogen distribution, fuel cells power units must include a fuel processor to generate hydrogen from available fuels. Those fuel processors are miniature chemical plants involving multiple catalytic steps. In the present contribution we describe the principles of fuel processor design and discuss the opportunities for catalyst research and development in this field.

Fuel processors produce hydrogen by reforming fossil fuels or alcohols to syngas. Because most PEM fuel cells have a very low tolerance for CO, a thorough cleanup of the reformatted product is required. There are two main routes to CO-free hydrogen: water-gas shift followed by selective oxidation of the residual CO, and membrane separation of the hydrogen in the reformatted stream. The first route requires three catalytic reactor units while the second, membrane separation, is in principle simpler requiring only one catalytic step, but it operates only at high pressures. Given the energy penalty involved in compressing gases, high-pressure systems are usually limited to liquid feeds only.

The first step in fuel processing is the reforming of the fuel. This is an endothermic, high-temperature process requiring a sizable heat input. In low-pressure systems the heat source can be separated from the process stream, as in steam reforming, or it can be part of the process reaction, as in autothermal reforming. Heat transfer from the heat source, usually a combustion unit, to the catalyst material can be rate and size limiting in steam reforming units. Heat transfer is facilitated in autothermal reformers because the heat of combustion is liberated next to the catalytic site where the reforming reaction takes place, but the price paid here is the dilution of the product hydrogen with atmospheric nitrogen. The size of these systems depends on the rate of the reforming reaction.

Chemical equilibrium mandates that the water-gas shift reactor be operated at low temperatures for maximum CO conversion. Yet, the rate of reaction drops to impractical low levels at the temperatures needed to achieve the low CO levels required by PEM fuel cell electrodes. Thus, the water-gas shift reaction is carried to a certain extent, and the residual CO is consumed in a selective oxidation unit. The selectivity of the CO oxidation increases as the temperature of the reaction decreases; hence high heat transfer rates are needed to obtain an effective CO cleanup without consuming a large fraction of hydrogen.

The combined size of the water-gas shift and selective oxidation units is a function of the CO level that the selective oxidation unit can accommodate. As the CO level increases, the size of the water-gas shift unit decreases, but the heat transfer duty on the selective oxidation reactor increases. Consequently, the ability of this reactor to transfer heat becomes the size-limiting parameter for the water-gas shift / selective oxidation CO cleanup process. In membrane units, the rate of hydrogen diffusion is the key parameter governing the size of the unit: as this rate increases, the required membrane area and pressure differential decrease.

METHANOL FUEL PROCESSING FOR FUEL CELL POWER SYSTEMS: CATALYSIS, KINETICS AND SYSTEM OPTIMIZATION

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Methanol is considered one of the most convenient fuels for fuel cell power systems because it can be processed at relatively low temperatures, compared to conventional hydrocarbons, and being a liquid it is much more easily stored and transported than gaseous fuels such as hydrogen or natural gas. It is readily produced from natural-gas feedstock but also can be produced from a variety of renewable feedstocks in particular through the pyrolysis of biomass such as fast growing woods. A number of fuel cell powered automobile and bus projects are based on methanol fuelled systems for example DaimlerChrysler NECAR and NEBUS and the GM Opel Zafir.

This presentation will discuss the work that has been done at the Royal Military College over the past twenty years on catalytic methanol-steam reforming. The process of going from catalyst development and selection to kinetic studies and finally to reactor design for system optimization will be described. It will be shown how the reactor design requirements for fuel cell power systems require a much more exact understanding of the catalytic reaction kinetics than conventional process industry reactor design. The requirements for catalysts with very specific properties will also be discussed. Finally, the mathematical simulation of methanol-fuel processors for fuel cell systems will be described showing the unique characteristics of the reactor operation in a fuel cell power system.

OXIDATION HETEROGENEOUS CATALYSIS FOR CLEAN PROCESSES

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Nowadays the increasing social pressure on industry to substitute traditional process by environmentally friendly technologies represents the most important driving force for the development of catalysts for fine chemicals.

Traditionally, fine and speciality chemicals have been produced predominantly using non catalytic organic synthesis; these processes can be characterized as follows:

- Relatively small scale production (5000 t per year)
- Stringent product specifications with high purity requirements
- Multifunctional molecules and materials
- Co-production of large amounts of unwanted products (stoichiometric oxidations with inorganic reagents)
- Utilizing of toxic or corrosive reagents
- Multistep processes resulting in lower overall yield of the desired product

In recent years, in this field, there has been a growing need for reduction of production price, increasing of product quality and performances, and substantial decreasing of waste. Moreover, the new industrial strategies demand to avoid the use of toxic raw materials and dangerous procedures and to decrease the consume of water and energy.

Since the manufacture of fine chemicals generally utilize thermally unstable reagents (heterogeneous catalysts are generally active at high temperature), involve multi-step reactions (with a consequent need of multi-functional catalysts) and employ big molecules that can not enter the catalyst porosity, there are a few problems to applying heterogeneous catalysis to this production.

Despite of this, the development of catalytic process on this field has received increasing attention. Different type of approaches have been used to achieve improved production process:

1. The development of catalyst active at lower temperature
2. The use of supports with large pores
3. The spreading of the active phase on the external surface of a support
4. The developments of new multifunctional catalysts
5. The use of low contact time at high temperature to avoid the decomposition of the product and of the reagents (short bed process)
6. The use of solvents to desorb the products or to orientate the intermediate formation
7. The encapsulation of supporting of homogeneous catalysts

A large number of oxidation reactions made possible by heterogeneous catalysts in principle can be applied to the synthesis of fine chemicals:

1. Reactions of oxygen insertion
    - Hydroxylation of aromatics
    - Olefins to epoxides
    - Alkylaromatics to aldehydes or ketones
    - Alkanes to alcohols
    - Amines oxidation
2. Oxidative dehydrogenation
    - Alcohol to aldehydes
    - Formation of double bonds
3. Nitrogen insertion with NH_3 and O_2
    - Ketones to oximes
    - Hydrocarbons to nitriles

However, quite many problems must be addressed in order to render a catalytic process technically viable, the following are the most important ones:

- Thermal stability of reagents and products (cleavage of c-c bonds)
- Presence of reactions of free radical oxidation

- Dissolution of metals (transformation to homogeneous catalysis) - Leaching

The various type of catalyst and oxidant that can be utilized are outlined in Table 1.

Catalyst	Oxidant
Transition metals dispersed in inert matrix (Es. TS-1)	H_2O_2/hydroperoxides
Noble metals supported (Es. Pd/Al_2O_3; Pt/Bi/C; Pd/C)	O_2
Supported polyoxometallates (Es. $H_3PW_{12}O_{40}/Al_2O_3$)	H_2O_2
Mixed Oxides	O_2/N_2O
Encapsulated complex in inert matrix	O_2/H_2O_2/hydroperoxides

While in bulk chemicals manufacture the choice of oxidant is largely restricted to molecular oxygen, the economics of fine chemicals production allow a broader choice of oxidants. Hydrogen peroxide is the preferred one due to its simplicity of operation but many other organic and inorganic oxygen donors can be utilized (hydroperoxide, N_2O etc.)

The choice of process (liquid phase versus gas phase) is largely dependent on the boiling point and thermal stability of the molecule in question. Where gas phase oxidation with O_2 is feasible this will probably be economically more attractive than other options.

Example from our laboratory

In the catalysis' laboratory of the University of Bologna there are several example of these new application of catalysis in the field of green chemistry, and particularly in the production of fine chemicals. These researches furnish some examples of the advantages given by the heterogeneous catalysis in the pollutants reduction and in the optimization of processes.

This example is:

The ammoximation of cyclohexanone in liquid phase made by titania-silica catalysts with the use of cyclohexanone, ammonia and hydrogen peroxide. As an example of oxidation reaction. In this reaction are not formed all the homogeneous by products as inorganic salts and it is possible, by the use of the TS-1 catalyst, to arise very high conversion of cyclohexanone and very high selectivity to the oxime product. The heterogeneous catalysis allows to use very mild reaction conditions and reagents very little dangerous. From our studies was possible to define more precisely the most probable reaction pathway and to understand the influence of some reaction and catalyst parameters, such as surface acidity and morphology and the presence of different titanium structures, that influence the formation of by products.

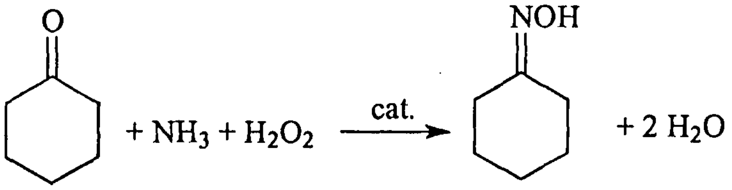

Fig. 1 Ammoximation of cyclohexanone

COUNTRY REPORT: BRAZIL

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Brazil is a developing country whose economy must grow at rates high enough so as to bring the income of its population to levels able to allow people to meet their needs. Industrial development must be conceived so as to foster the growth of national income while simultaneously protecting the environment and the quality of life. Catalytic clean technologies play a very important role within this framework and the Brazilian academic community is increasingly getting involved with policies aimed at to reach this goal.

Development of catalysts for the control of emissions from both stationary and mobile sources is a concern of many groups working in fields such as abatement of VOCs (chlorine-containing compounds, aromatics, various solvents), wastewater treatment, NOx/CO removal from exhaust gases from vehicles (specially in the case of engines driven by sulfur/nitrogen-rich fuels, natural gas or ethanol/petrol blends), SOx/NOx removal from the regenerator of FCC units, and reduction of NOx emissions during natural gas combustion for the generation of electric power.

Obtaining fuels with reduced levels of contaminants is another approach involving catalysts to produce them from natural gas, either through direct or indirect routes, from vegetable oils, or for hydrotreating various refinery streams.

To substitute current technologies by more environmentally friendly ones is the driving force for those dealing with, for instance, the use of heteropolyacid catalysts for the bleaching of pulps without the use of chlorine, the substitution of heterogeneous catalysts (acidic, basic, redox) for homogeneous ones, and the use of two-phase catalysis to avoid the use of organic solvents.

In the case of a large tropical country such as Brazil, the use of renewable sources, specially those obtained from agriculture, is necessarily a main concern. Examples in this area are the use of ethanol to produce hydrogen for fuel cells, to produce acetic acid from ethanol in a single-step process, and the synthesis of fine chemicals from essential oils or carbohydrates.

Finally, recycling and catalytic transformation of spent polymeric materials is also an approach undertaken to reduce the disposal of solid wastes.

COUNTRY REPORT: COLOMBIA
ACTIVITIES OF THE COLOMBIAN RESEARCH GROUPS IN CATALYSIS

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In the last decade, environmental catalysis has been increasingly considered in Colombian academic catalyst research. Catalytic approaches infuse both basic and applied research, as chemists and engineers seek the application of catalytic techniques to cleaning up a wide variety of existing problems, and apply catalysis in the design of benign processes that will eliminate or minimize pollution in the first place.

Colombian basic research in catalysis ranges from the synthesis and characterization of new crystallized or organized porous solids and oxides, to adsorption mechanisms developed through a theoretical analysis and modeling of the adsorption data on these materials. Colombia applied research in catalysis is distributed among numerous projects, such as acid catalysis, bifunctional metal/acid catalysis, and redox catalysis. Much work is done using acid or metal zeolite catalysts, which, are mainly involved in refining (cracking, hydroisomerization, hydrocracking), fine chemical synthesis (oxidation, epoxidation and hydroxylation of organic molecules) and depollution (elimination of NOx and VOCs). Researchers are also active in developing catalytic combustion processes that emit no nitrogen oxides, reducing the sulfur and aromatic content of fuels; curtailing byproduct production in fluid-catalytic cracking units; oxidizing or hydrodechlorinating emissions of chlorinated hydrocarbons and evaluating catalysts for Fisher Tropsch chemistry and CO/CO_2 hydrogenation.

An area of growing interest in Colombian research is heterogeneous photocatalysis as a new efficient (and cheap) way to decontaminate toxic waters either with artificial light or by solar detoxification, for producing clean (drink) water. Many toxic inorganic ions containing S, N, C and P are oxidized into their harmless upper oxidized state. Heavy (noble) metal cations can be reduced by the photoelectrons and then photodeposited on titania as crystallites without screening its photosensitive surface. Most of aliphatic and aromatic pollutants, as well as, more complex molecules such as pesticides (herbicides, insecticides, fungicides, etc.) and surfactants dyes are totally mineralized into CO_2 and innocuous inorganic anions.

In this contribution, a list of the Colombian research teams involved in catalysis, highlighting their field of expertise, will first be presented. Then, we will focus more on the activities of our environmental catalysis research group at "Universidad de Antioquia".

COUNTRY REPORT: URUGUAY
POTENTIAL DEVELOPING OF NOVEL CATALYTIC MATERIALS FOR SUSTAINABLE INDUSTRIAL PROCESSES IN URUGUAY.

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Several research activities dealing with heterogeneous catalysis applied to environmental topics have been performed in our country since twenty years ago. The objectives of these works are strongly related with national and regional characteristics of industrial activities. Among the principal research projects are the following:

-Catalytic biomass pyrolysis for valorization of residues from the forestry industry. The specific objective is the obtention of gas mixtures for their use as fuel and as synthesis gas for production of valuable organic compounds (isoparafynes, alcohols, olefins, aromatics).

-Catalytic gasification of wastes for remediation of wastes of thermal pyrolysis of wood. The specific objective is the elimination of hazardous liquid and solid residues and obtention of gas mixtures.

-Heterogeneous photocatalysis applied to water decontamination. The main objective is the application of semiconductor materials to the removal of heavy metals and hazardous organic compounds from wastewaters. Some specific objectives are the removal of mercury compounds from wastes of alkali plants and the destruction of pesticide residues.

Some other research activities deals with the study of novel catalytic materials for industrial processes such as:

-Oxidative dehydrogenation of hydrocarbons. The specific objective is the transformation of light hydrocarbons into ofefins and oxygenated products.

-Catalytic transformation of ethanol coming from aqueous solutions derived from biomass fermentation. The specific objective is the selective transformation of bioethanol into valuable chemical products such as acetone, acetaldehyde and other organic compounds.

-Catalytic transformation of essential oils for the obtention of valuable chemical products. One specific objective is the study of limonene transformation into epoxyde, alcohols and cetones derivates.

Different catalytic solid materials have been employed for all these research activities. The details of their preparation and performance will be exposed.

Some other research projects are focused on the preparation of catalytic materials such as:

-Activated carbon from wood residues.

-Pillared clays from national clay mineral resources.

An assessment of all these activities will also be exposed in order to planify future new research activities.

CATALYTIC TECHNOLOGIES FOR WATER DEPOLLUTION

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Catalysis is a key technology to provide realistic solutions to many environmental issues. A new area of growing interest is related to the use of catalytic technologies for the abatement of water pollutants, the treatment of wastewater or the improvement of quality of drinking of industrial water. Water and wastewater treatment has become a major social, technological, economical, and political problem. Legislation in every country imposes environmental regulations and health quality standards that steadily become more restrictive. Sludge disposal poses additional problems.

Water and wastewater treatment requires usually several combined methods, but catalytic technologies may contribute to improve the overall process, especially when (i) not or hardly biodegradable chemicals are present, (ii) more compact technologies are required and (iii) selective or higher conversion levels are need. This lecture will report about the use of catalytic technologies in advanced water treatments. First some general question of the opportunities, prospects and problems in this new field of research will be discussed, and then some specific examples related to the problem of recycling water in electronic industries and treating agro/food industrial effluents will be analyzed.

Catalytic methods were not widely applied in water treatment up to now, although some examples of industrial processes exist, especially regarding catalytic wet air oxidation processes. After an introduction on the problem of water and its industrial use, the use of catalysts to improve wet air oxidation processes is discussed. Emphasis is given on industrial processes and the new question of sludge treatment. New advanced oxidation processes are also briefly commented. Reductive processes in water treatment will be later also discussed and specifically the problem of denitrification and chlorinated hydrocarbon conversion using H_2 and a catalytic membrane reactor. The general question of water remediation technologies will be analyzed in reference to this problematic with some observation also on the question of water remediation by MTBE contamination.

The second part of the lecture discusses two specific examples and the question of reducing wastewater. The shortage of ground and underground water in several areas of the world together with the increasing sensibility to the problem of landfill large volumes of water even if containing low amounts of organic products has put in evidence the question of developing efficient technologies for water purification so as to recycle industrial rinse water. This problem is especially critical in electronic industries where large volumes of high-quality water is required and large volumes of rinse water containing a great variety of chemicals are produced in all metal-finishing processes. In these cases, the use of efficient technologies for rinse water purification not only lead to a benefit for environment, but can also reflect in an economic benefit for the process, being the cost of recycled water lower than that of city water plus the necessary treatment necessary to achieve the required level of purity. The recycle of rinse water must be thus viewed as an opportunity for chemical and non-chemical industries more than a necessity imposed from environmental regulations.

A second case discussed regards the problem of wastewater from agro/food production. As example, the case of olive oil mills wastewater is discussed, which is a relevant environmental problem due to the presence of phytotoxic chemicals such as polyphenols. However, various other wastewater emissions from agro/food production have similar characteristics. The use of catalytic technologies allow to improve process performances and manageability.

The research in the area of catalysts for water and wastewater treatment is at the beginning, but good prospects for research and application exist. It must be emphasized, however, the necessity of developing specific catalysts and new engineering solutions which, on the other hand, may open new opportunities also for fundamental and applied research in other fields of catalysis.

CATALYTIC TECHNOLOGIES FOR PREVENTION/CONTROL OF AIR POLLUTION FROM MOBILE SOURCES:
- END OF PIPE STRATEGIES (TWC & DENOX)
- NEW CLEAN FUELS (HYDROGEN PRODUCTION)

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The problem of reducing the air pollution from mobile sources will be tackled from two points of view: the use of end-of-pipe technology (three-way and DeNOx catalysts) and the development of new clean fuels (hydrogen).

A brief review of the history of the autocatalyst, culminating in a discussion of current state of the art catalyst systems will be given. Since the 70's, three-way catalysts (TWCs) have been successfully used in the USA to reduce emissions of the pollutants contained in automotive exhausts. NO_x can be transformed by a reduction process to the harmless N_2, while removal of unburned hydrocarbons and CO requires an oxidation to CO_2 and H_2O. These two processes have to occur simultaneous. The conversion efficiency of these systems strongly depends on the operating conditions of the engine and in particular on the air-to-fuel ratio (A/F) over the catalyst. In fact, high and simultaneous conversion of all three classes of pollutant is obtained only under stochiometric A/F ratio, while oxidising (lean) or reducing (rich) conditions significantly decrease the efficiency of the converters. One of the main drawbacks of the actual systems is the fact that they do not have any catalytic activity below 300/350°C. This implies that during a cold-start, the emission of pollutants is high until the catalyst has reached the working temperature. The significant improvement of the performance of the converters obtained by introducing ceria-zirconia mixed oxides as new additives/promoters in the formulation of three-way catalysts will be discussed. These systems can act as excellent oxygen buffering systems, ensuring a fine control of the air to fuel ratio over the catalyst and therefore enhancing the conversion efficiency. Moreover, CeO_2-ZrO_2 solid solutions show a better thermal stability with respect to the previous type of oxygen storage promoters.

The desire to improve the fuel economy of combustion engines has increased interest in the use of lean burn engines. However, as indicated above, running an engine under lean conditions prevents the reduction of NO_x on conventional TWC, since much of the hydrocarbons in the exhaust are oxidized by oxygen over such a catalyst. Literally hundreds of catalysts have been tested in the search for an efficient lean burn system; transition metal-containing zeolites and Pt/Al_2O_3 being among the most effective known materials. They, however, suffer from respectively poor hydrothermal stability and a narrow range of activity (200-270°C). Ag containing catalysts have recently attracted attention as inexpensive - compared to Pt catalysts- and highly active systems. A different approach to the NO conversion under oxidizing conditions is based on the NO_x storage concept, where NO_x is stored in the catalyst during lean periods and during short rich intervals the NO_x is released and reduced.

Finally the concept of new clean fuels, with particular attention to hydrogen, will be briefly discussed. In principle, the prevention of air pollution is certainly better than the post-combustion control. The problems related to hydrogen production, distribution and storage, which are slowing down the use of fuel cells, will be addressed.

COUNTRY REPORT: MEXICO
COMPARATIVE STUDY ON THE ACTUAL TRENDS OF R&D PROJECTS AND MARKET NEEDS IN THE REFINING INDUSTRY OF MEXICO

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A recent study was made on the main opportunities in the refining catalyst market in Mexico, which indicates the influence of new environmental regulation laws and the continuous quality degradation of crude oil in terms of °API , % wt. S, %V, and %Ni respectively. Then, a comparison study is presented here on the R&D programs and the refining industry needs in Mexico. The Petroleum Institute of Mexico (IMP) contributes significantly to generate the catalysts technology used in the domestic refining industry at Pemex, which represents about 2 % of the global worldwide market (i.e. in a monetary basis). Apart the R&D projects directed to obtaining incremental benefits in the main refining processes (FCC, HDT, Reforming), innovative research on new catalytic materials is considered too, that is about 10 % of the overall catalysts R&D portfolio at IMP, for example (1) Isoparaffins alkylation by solid acid catalysts, (2) Hydrogen recovery from waste products and (3) Catalysts for production of low sulfur gasoline and diesel. Also, the impact of new strategies for R&D is discussed, in particular the Combinatorial Catalysis. On the other hand, the academic sector is composed by several groups across the country working on different topics related to actual trends of the literature, for example (1) NOx reduction with light hydrocarbons, (2) Supported metal catalysts for hydrogenation reactions, (3) Zeolites synthesis and catalytic technology related with, and (4) Hydrocarbons oxidation. In this respect, there is a steady contribution of the catalysis groups to scientific publications in most of the catalysis journals.

CATALYTIC TECHNOLOGIES FOR SUSTAINABLE INDUSTRIAL PROCESSES: THE ROLE OF PDVSA- INTEVEP

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The strict environmental restrictions in the compositions and quality of transportation fuels are the new challenge that refining catalyst industry has to face. The fuel molecular composition is recovering a great importance. In the past, boiling point range and the fuel performance were the main measures of fuel quality. Industrial development, therefore, requires products that minimize emissions of toxic substances. Moreover, regulations for fuels are increasing in severity. Gasoline and diesel specifications have been changed in several countries. For example, the gasoline specification sulfur will be 30 wt ppm while from diesel (ULSD) will be 15 wtppm in USA during the 2005-2006. The diesel sulfur regulation will change at 50 wt ppm in Europe in 2005. Other aspect to be considered is a new fuel without sulfur, aromatic and olefins, which will be used as a source of energy in the vehicles based on fuel cells. The role of Intevep to improve the catalytic technologies for sustainable refining processes has been based on the market position, product quality adjustment produced according to requirements and cost optimization. As a result, we have identified technological opportunities: based on sulfur reduction technologies, residue and heavy crude conversion technologies and new fuel formulations. Currently, we are focused on the development of new types of catalytic materials to reduce the sulfur in gasoline and diesel aiming to improve fuel quality, catalytic technologies for increasing petrochemical value of C_5 naphtas, new FCC catalytic additive to optimize octane-barrel and the production of alkylate and petrochemical feedstocks and the new catalyst for hydrogen production. All of the catalytic research is developed on new concepts where catalyst preparation is based on the structure control of catalyst support and the selective addition of the active agents.

CATALYTIC TECHNOLOGIES FOR SUSTAINABLE INDUSTRIAL PROCESSES: THE ROLE OF PETROBRAS

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In 1997 a new law was introduced in Brazil setting that a small percentage of the petroleum production royalties is to be applied in science and technology programs,. coordinated by local universities and research centres. The program has attracted a number of petroleum and gas companies to establish joint programs with these institutions and is gradually changing the panorama of science and technology in the country.

After a period of adaptation, the parts involved (government, industry and academia) are starting to interact efficiently. The new law has considerably increased the interactions between petroleum engineers, businessmen and researchers, setting new levels of efficiency and environmental concern for the local industry. New jobs and business opportunities have also been created.

Gas-to-liquid (GTL) processes are a good example of results obtained with this model. Either to monetize stranded natural gas reserves, to develop new fuels and lubricating oils or simply because of the new environmental concerns, it is well known that companies all over the world are developing their own GTL programs, independently or in cooperation with technology partners. Regardless of being very intense and important, the participation of academic institutions in this effort has been mostly indirect. In Brazil, however, the royalties program mentioned above has been used to start a direct cooperation in GTL technologies with a number of academic institutions. Each partner is responsible for a different aspect of the technology such as catalyst development (for Fischer-Tropsch synthesis, autothermal reform, direct conversion of methane to other hydrocarbon forms, etc.), use of CFD techniques to develop slurry and other reactor models and the analysis of alternative oxygen fractionation methods. It is worth mentioning that all those projects will be developed under the supervision of the Petrobras technical staff.This rather innovative research model has revealed itself as an interesting alternative for the management of limited science and technology resources in developing nations.

Furthermore, the role of the refining policy of Petrobras regarding sulphur reduction in different fractions such as diesel oil and gasoline is discussed. Sulphur contents in gasoline and diesel must be reduced to 50 ppm in 2004, tending to reach very low levels (4-5 ppm) in a near future. Such levels can only be attained should higher process temperatures (+ 38°C) and a catalyst four times more active be employed (table 1), not to mention high investments.

Table 1 – Sulphur reduction

S (ppm)	Catalytic activity	Process temperature (°C)
500	100	Base
350	130	+7
200	190	+17
100	300	+29
50	420	+38

The quest for technological break-troughs in the field of catalysis is therefore necessary. Characterisation of new catalytic systems, using "in situ" technologies, as well as studies on catalyst deactivation (modeling and evaluation) ought to be carried out. Moreover, hydrodynamic experiments, aiming at a better feedstock distribution in the reactor have to be performed. Finally, alternative technologies such as adsorption, extraction, biorefining, supercritical hydrogenation and plasma should not be disregarded.

CATALYTIC TECHNOLOGIES FOR THE CONVERSION OF RENEWABLE RESOURCES

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There are strong incentives to develop chemical processes starting from biosustainable resources (e.g., carbohydrate- or triglyceride-containing crops), which in contrast with petroleum-derived feedstocks are renewable and contribute to decrease CO_2 emissions. These raw materials consisting of highly functionalized molecules can be converted by clean catalytic processes into highly priced derivatives used as food additives, and specialties or fine chemicals. In this lecture, a general survey of catalytic transformations of crop-derived feedstocks will be given. Then, a few examples of metal-catalyzed conversion of carbohydrates obtained from maize or other starch-containing crops will be described.

Hydrogenation reactions: (i) Batch hydrogenation of glucose or fructose on nickel catalysts into C_6 polyols used in food and chemical industry have been replaced by continuous processes using promoted, ruthenium-based catalysts allowing superior activity, selectivity and stability with time. (ii) High value-added C_5 and C_4 polyols can be obtained from cheap C_6 carbohydrates by oxidative decarbonylation followed by hydrogenation of aldonic acids and aldonolactones. Thus, the hydrogenation of arabinonic acid and corresponding lactones into arabitol was conducted under very moderate reaction conditions on promoted ruthenium catalysts resulting in a 98% yield. (iii) Carbohydrates were dehydroxylated under hydrogen pressure on CuO-ZnO catalysts mainly into C_6 triols and tetrols, or dehydrocylized into polyhydric cyclic ethers on supported palladium catalysts. These polyols blends are useful for the manufacture of polyesters or alkyd resins employed in the manufacture of paints.

Oxidation reactions: There is a great interest in the oxidation of aqueous solutions of carbohydrates with air on supported metal catalysts because these catalytic reactions are environmentally safe and economically attractive; they could advantageously replace stoichiometric or enzymatic oxidations. Several examples of highly selective oxidation processes of monosaccharides (glucose), or di-saccharides (sucrose, lactose) in the presence of bismuth-promoted palladium or platinum catalysts will be discussed.

Catalytic modifications of starch : Native or partially degraded starch can be incorporated in various manufactured products (e.g., polymers, paper, paints) provided the polymeric chains are chemically modified either to increase or to decrease starch hydrophilicity. (i) Soluble organometallic catalysts have been employed to catalyze the oxidation with hydrogen peroxide of starch chains (diol clivage) in order to increase starch hydrophilicity. (ii) In contrast, aliphatic chains have been grafted on starch by telomerization of butadiene on OH groups catalysed by soluble palladium complexes.

PRODUCTION OF HYDROGEN AND OXYGENATES FROM BIOETHANOL

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The use of bioethanol as feedstock reduces the net emission of greenhouse effect gases since, analyzing the complete cycle of this alcohol, the total production of carbon dioxide is practically null. In addition, it helps the economic development of rural areas from Latin America because of two fundamental aspects: a) the places where the conversion is carried out must be near the biomass resources given that the profitability of the process highly depends of the transport cost of raw material, and b) the integrated production of food, fuels and other by-products will help the industrial stability affected by the fluctuations of the market.

The production of hydrogen from bioethanol is being carried out in our laboratories using copper, nickel, magnesium and alumina catalysts and a commercial catalyst based on copper, zinc and alumina. Acceptable yields of hydrogen and total conversion of ethanol have been achieved operating at atmospheric pressure, in a temperature range of 300-500°C, and water/ethanol ratio of 0-9. The previous thermal treatment and the metallic load significantly affect the performance of the catalysts. The formation of hydrotalcite type compounds has been detected. A possible reaction mechanism over different active sites is proposed.

In the last years experimental research has shown the possibility of using acetal (1,1 diethoxyethane) as an oxygenated additive for gas-oil. Working in an international project sponsored by CYTED, in which several groups from different iberoamerican countries are participating, the basic engineering for the production of acetal from bioethanol and acetaldehyde has been developed. The synthesis is carried out at atmospheric pressure and room temperature using solid acid catalysts in replacement of the traditional liquid ones. Several catalyst (zeolites, FCC catalysts, alumina, resins) have been tested and most of them showed high selectivity and activity being the sulfonic ion exchange resin the most active and stable at the used operation conditions. The addition of an extractive solvent is convenient since it increases the equilibrium conversion and simplifies the product purification, which must be free of water for its use as an oxygenated additive. A basic engineering using a fixed bed reactor is proposed.

ACID AND REDOX ZEOLITES IN FINE CHEMICALS SYNTHESIS. RELATIONSHIP BETWEEN CATALYSIS, ACTIVES SITES AND SURFACE PROPERTIES

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The advantages of heterogeneous catalysts, including zeolites, are largely demonstrated in bulk chemicals and refining areas. Much different is the situation in fine chemical industry, where the traditional tools of organic chemistry are preferred. However, two rapidly growing areas of research, in the last decade, are organic reactions in which acid and redox zeolites are employed as catalysts. The close relation of these studies with a tendency towards alternative routes for fine chemical synthesis is apparent.

The use of acid zeolites allows the reduction of wastes, the replacement of volatile hazardous acids (HF, BF_3), the prevention of plant corrosion. Accordingly, several studies deal with the application of acid zeolites to aromatic acylation, a reaction in which more than stoichiometric amounts of metal halides and strong mineral acids are traditionally employed. Other reactions studied are the alkylation/hydroxyalkylation of aromatic and heterocyclic compounds, the reactions of isomerization, esterification, hydration, chlorination and many others. Besides the usual advantages of heterogeneous catalysis, the attractiveness of acid zeolites results also from the variety of structures and pore dimensions, and from the possibility of fine tuning acid and surface properties.

In the area of catalytic oxidations, the role of hydrogen peroxide has steadily increased, driven by two converging events, *i.e.*, the discovery of new and effective catalysts, particularly redox molecular sieves, and the growing interest for clean technologies. Zeolite catalysts are wholly inorganic materials, inherently stable to oxidative degradation in contrast to organometallic ones. Their number increased rapidly throughout the 1990s, providing a multiplicity of (potential) catalysts characterised by a variety of compositions, structures and porosities. They catalyse the epoxidation of olefins, the hydroxylation of aliphatic and aromatic C-H bonds, the ammoximation of cylohexanone, the oxidation of O-, N- and S-compounds with hydrogen peroxide.

Both classes of zeolitic catalysts show similarities and dissimilarities with related homogeneous systems, *i.e.*, soluble strong acids and peroxidic oxidants. Their properties are not only dependent on active sites, but influenced also, and to a major extent, by surface characteristics. The aim of the presentation will be to discuss the relationship between activity and selectivity, from one side, and the nature of active sites and adsorption phenomena, from the other. Relevant examples taken from liquid phase reactions, catalysed by acid and redox zeolites, will be examined to this end.

PARTIAL OXIDATION AND MIXED REFORMING PROCESSES FOR SYNGAS PRODUCTION

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Syngas, and particularly H_2 obtention, has gained a great importance in the last few years, due to a series of convergent reasons: i) increase of hydrogen demand in refining plants; ii) use of hydrogen as a source of clean energy (fuel cells, automobiles, etc.); iii) Process of transmission and chemical energy storage. Syngas is mainly produced via natural gas steam reforming (SR); this process has the drawback of its high energy cost and harmful environmental effects. Partial oxidation of methane (POM), dry reforming with CO_2 (DR) and a mixed reforming with O_2 and CO_2 (MR) are alternative routes, both energetically and environmentally attractive[1]. Transition metals are active and selective catalysts for these reactions. Due to the relatively severe operating conditions under which these reactions are held (600-750 °C, low H/C and O/C ratios), these systems present stability problems, with respect to sintering and carbon deposits[2].

Research works carried out by our group[3], employing Ni catalysts on α-Al_2O_3 based supports, showed that: i) the addition of a layer of aluminum oxide diminishes the rate of sintering of Ni catalysts. In this sense, another possibility is the use of other supports (CaO, La_2O_3, MgO, ZrO_2); ii) the utilization of organometallic precursor compounds (Ni acetylacetonate) give rise to systems with a higher resistance to carbon formation, compare to catalysts prepared using conventional precursors (Ni nitrate); nevertheless, it is not possible to completely inhibit this phenomenon. The use of supports with basic properties (MgO, CaO, ZrO_2) show a noticeable increment in the resistance to carbon formation; iii) the addition of metallic promoters (for instance the addition of Sn via SOMC/M), modifying the nature of the nickel active sites, are able to decrease the carbon reaction rate. In this case, the effect of the metallic promoter can be explained by means of the increase in the CO_2 adsorption capacity, leading to high concentrations of chemisorbed oxidic phases (O-S, generated from the adsorption: $CO_2 + 2S \rightarrow CO\text{-}S + O\text{-}S$; S: active site) in the metal-support interphase, which can react with CH_x-S species, originated in the dissociative adsorption of CH_4 ($CH_4 + (5-x)S \rightarrow CH_x\text{-}S + (4-x)H\text{-}S$), giving rise to the formation of CO and H_2 ($CH_x\text{-}S + x\ O\text{-}S \rightarrow CO\text{-}S + x\ H\text{-}S$).

The study of these reactions employing model catalysts, will help to the comprehension of the successive steps leading to the obtention of hydrogen. There are different types of model supports, such as α-Al_2O_3, TiO_2, SiO_2, ZnO, ZrO_2, and at the time being, there are many techniques that allow the deposit of a catalytic active phase on these supports, in order to generate a model catalyst. With these tools, well-defined catalytic phases can be obtain, which, in turn, have similarities with conventional supported metallic catalysts.

Our research group propose the following activities for the next period:

a) Preparation and characterization of supported metallic catalysts (M/S, MM'/S, where S can be: α-Al_2O_3, ZrO_2; supports modified by the addition of Ce; M: Ni, Ru, Pt; M': Sn, Ge). The supported metallic phase will be prepared employing two different precursors: inorganic and organometallic compounds. A very important topic will be the preparation of bimetallic systems, using SOMC/M techniques.

b) Characterization of the catalytic phases obtained, by TPR, TPD, XRD, IR-DRIFTS, Atomic Absorption, TEM/EDX, gas chemisorption, XPS and EXAFS/XANES.

c) Analysis of the catalytic properties (activity, selectivity and stability) of the catalysts prepared in item a), in the syngas obtention reaction from methane (via POM, DR and MR). Carbon formation will be analyzed by TGA/DSC.

d) Preparation of model supports and deposit of the active phases on them.

e) Analysis of the reaction kinetics of the "real" catalysts (determination of reaction order, activation energy and reaction mechanism) and of model catalysts.

Special emphasis will be put to link the behavior and performance of model and "real" catalysts. The objective of these studies is to obtain knowledge on the mechanism of C-H activation and on the nature of intermediate chemisorbed species, in order to state the role that they play in the transformation of methane to syngas using sustainable technologies. We will also study the deactivation mechanism by carbon formation, which is very important for DR, POM and MR reactions.

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THE IMPACT OF THE LIBERALISATION OF THE ELECTRICITY MARKET ON ITS ENVIRONMENTAL PERFORMANCE FOR SELECTED COUNTRIES OF LATIN AMERICA AND EUROPE

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Competitive electricity trade is a relatively new phenomenon. The parties on the market are still learning how to adjust to the conditions. At the same time, gradual and continuous improvements of the regulations are taking place.

The European Commission has recently approved the Concerted Actions for a *Discussion Group on Environmental Policy Instruments in Latin American and European Liberalised Electricity Markets.* A consortium of nine institutions from Argentina, Brazil, Chile, Germany, Spain and The Netherlands was formed to undertake the activities involved in the project. Research institutions of all countries, the regulatory agencies of Argentina and Spain together with the Pan American Health Organisation conform the consortium.

The main objective of the project is focused on the improvement of the design of policies for the promotion of environmentally friendly electricity systems in Europe and South America while allowing for liberalisation and growth of this sector. A series of tasks were designed to accomplish this goal. They concern: 1) the review of the effects of liberalisation on the environmental impact of electricity systems; 2) the analysis and comparison of methodologies for the assessment of the environmental impact of electricity systems; and 3) the exchange of experiences on the incorporation of environmental aspects into liberalised electricity markets.

Through a series of meetings, in which the work carried out and the views of the research institutes and regulatory bodies will be presented and discussed, the current environmental, economic and policy conditions of the electricity sector in the participating countries will be identified. The expected effects that liberalisation may cause in these conditions and the most adequate measures to be implemented in order to favour progress in sustainable development in this sector will be also discussed.

The major outcome of the concerted action will be a set of recommendations for decision-makers both in South America and Europe about the consequences on the environment and on the economy of the liberalisation of the electricity sector. It is also expected that the group will identify the most adequate policies to be pursued in order to attain a sustainable development of the electricity sector.

The first meeting of the Project was held in Santiago, Chile on September 2001. In this talk we will briefly present the key issues of the liberalisation process in each of the six countries, pointing out to main similarities and differences. We will also discuss the major trends on the impact on the environmental performance of the different electricity sectors that has been thus far identified.

Workshop on

Catalytic Technologies for Sustainable Industrial Processes

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Chemical Engineering Department of University of Buenos Aires

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