Department of Chemical Engineering
University of Castilla-La Mancha

HETEROGENEOUS CATALYSIS

Laboratory of

Heterogeneous Catalysis

DEPARTMENT OF CHEMICAL ENGINEERING

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Department of Chemical Engineering

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The Department of Chemical Engineering at UCLM was established in 1990 with four permanent professors. After fourteen years, the staff is constituted by more than forty people working and teaching in different aspects of the Chemical Engineering Science.

The Department of Chemical Engineering at UCLM has currently different research interests based on the development of solid catalysts, design of chemical processes, theoretical study of the mass transfer, management of waste waters (through electrochemical, membrane and aerobic and anaerobic treatments) and improvement of polimerization processes of industrial interest.

An important part of the research is contracted by Spanish and, occasionally, European companies. Likewise, there is an important contribution of basic research, which has been founded by European, Spanish and regional institutions.

There is a constant flow of researchers from this Department to different European and America Universities. We have permanent contacts with the Universities of Kentucky (U.S.A.), Newcastle (U.K.), Utrecht and Delft (The Netherlands), Salerno (Italy) and Zurich (Switzerland).

As a consequence of the research activity developed in the period ranged from 1998 to 2004, the following results can be shown:

- Archival publications: 112.
- Research theses (completed): 13.
- Posters and conference presentations: 245.
- Funds obtained from research projects: 5,2 MM €.

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HETEROGENOUS CATALYSIS

1.1. AIMS

- Preparation of catalysts (lab and pilot plant scales).
- Characterization of solid catalysts.
- Study of catalytic reactions (gas and liquid phase).

1.2. STAFF

- Dr. Antonio de Lucas
- Dr. José Luis Valverde
- Dr. Paula Sánchez
- Dr. Fernando Dorado
- Dr. Amaya Romero
- BS. María Jesús Ramos
- BS. Agustín Garrido
- BS. Antonia Fúnez
- BS. Prado Belén García
- BS. Antonio de Lucas

1.3. ON-GOING PROJECTS

- *Catalytic synthesis and characterization of carbon nanofibres and nanotubes*

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are graphitic filaments with diameters ranging from 0.4 to 500 nm. CNTs and CNFs have become one of the most active fields of nanoscience and nanotechnology due to their exceptional properties that make them suitable for many potential applications as polymer reinforcements for composites or breakthrough materials for energy storage, electronics and catalyst supports. The outline of this work is to develop a synthesis method to prepare CNFs for their further use as a catalyst support. These materials are being synthesized by Chemical Vapor Deposition using C_2H_4/H_2 feedstock metal supported catalysts. As supports, zeolites, pillared clays, SiO_2, are being used. Different parameters of synthesis are being studied in order to control the yield and the characteristics of the ultimate products.

- *Electrochemical promotion studies in the catalytic reduction of NO_x*

The catalytic activity and selectivity of metals interfaced with solid electrolytes can be altered dramatically and reversibly via potential application. The increase in catalytic rate can be several orders of magnitude higher than that anticipated from Faraday's Law. This new phenomenon of electrochemical promotion or NEMCA effect is of considerable theoretical and potentially practical importance in heterogeneous catalysis.

- *SCR of NO_x over PILCs*

The nitrogen oxides are the source of severe environmental problems. An emission control method NO_x is the Selective Catalytic Reduction (SCR) using hydrocarbon or alcohols as reducing agents. In this research, hydrocarbon or alcohols, as the reductant compounds, are used over pillared clays. Pillaring clays (PILCs) are two-dimensional materials prepared by exchanging charge-compensating cations between the clay layers with large inorganic metal hydroxycations that are oligomeric and are formed by hydrolysis of metal oxides or salts. After calcination, the metal hydroxycation are decomposed into oxide pillars that keep the clay layers apart and create interlayer and interpillar spaces, exposing the internal surfaces of the clay layers.

- *n-Octane hydroisomerization in liquid phase*

Reformulated gasolines must keep a high-octane rating with reduced aromatic and olefin content. In the production of gasoline from naphtha, C5 and C6 n-paraffins are isomerized to their branched isomer. Larger paraffins are used for catalytic reforming. Isomerization of paraffins larger than C6 is a way to improve octane rating without increasing the aromatic or olefin content. Batch hydroisomerization of n-octane in liquid phase was carried out in a stirred autoclave reactor using different Pt or Pd-zeolite as the catalyst. Liquid phase conditions were kept at the reaction temperature of 250ºC and the pressure of 100 bar. The vessel was filled with the desired n-octane volume and 2g of catalyst were charged and then pressurized with hydrogen. Samples of the gas effluent and the liquid phase were collected periodically and analyzed by capillary GC and GC-MS, respectively.

- *Isomerization of parafinic fraction (C7-C8) as an alternative to the catalytic reforming*

The current environmental requirements demand the production of gasoline with the minimum content in compounds considered harmful to the environment or the public health, causing an important decrease of the octane number of gasolines. The processes of n-paraffin hydroisomerization needs the presence of bifunctional catalysts. In this work, the acid function is provided by a zeolite and the hydrogenating function is provided by a noble metal (Pd and Pt). The technologically alternative more interesting is the production of branched paraffin with high octane number. If a zeolite based catalyst is to be used to industrial level, it would be necessary to pelletize it with a binder in order to obtain larger and more resistant particles, and to avoid an extremely high pressure drop in fixed-bed reactors. The aim of this work is to develop an useful catalyst to isomerize heavy naphtha in order to obtain a product with high octane number.

1.4. EQUIPMENT

- Lab and pilot plant set-up for the catalysts preparation.
- Liquid and gas phase lab reactors (some of them can operate at pressures above 50 atm)

- Characterization techniques:
  - TPD/TPR
  - BET
  - TGA/DTG
  - DRS FT-IR. Catalytic chamber is included in the facility.
  - XRD
  - SEM
  - DRS UV-vis.
  - Gas chromatography.
  - Size determination by laser dispersion.
  - GC-MS.
  - Atomic absorption and ICP
  - Sample digestion by microwave.

The rest of characterization techniques (RAMAN, TEM, etc.) uses to be contracted to the external services of relevant Spanish universities.

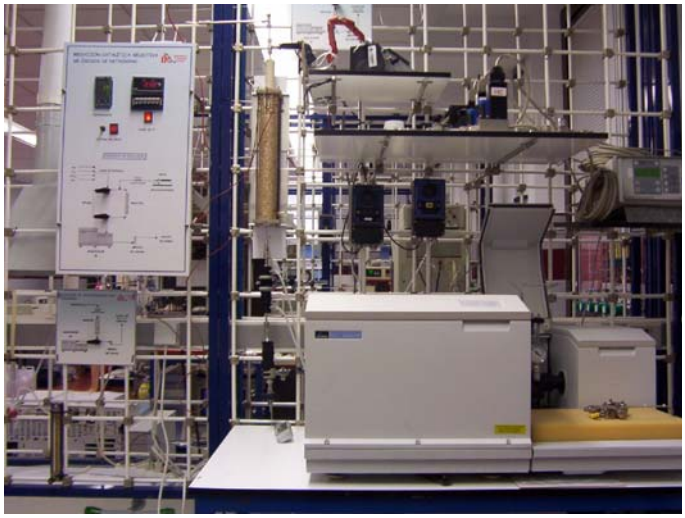
1.5. SOME RELEVANT RESEARCH PROJECTS (1998-2004).

- Project founded by the Spanish government (C.I.C.Y.T. AMB-96-0436). *SCR of NO_X using hydrocarbons as reductants.* A. de Lucas, P. Cañizares, L. Rodriguez, J.L. Valverde, J. Rincón, P. Sánchez, F. Dorado, A. Carrero y C. Molina. July 1996-September 2000.

- Project founded by the European Union (ENK5-CT-1999-00001). *Catalytic Abatement of N_2O and NO_x from Combustion Power Plants.* J. Otero, A. de Lucas, J.L. Valverde, F. Dorado, I. Asencio, J. Figueiredol, I. Vasalos, I. Colbeck, W. Reschetilowski. January 2000-December 2002.

- Project founded by the Spanish government (PPQ2001-1195-C02-01). *Isomerization of paraffinic fractions (C7-C8) as an alternative to catalytic reforming: bifunctional catalyst development and pilot plant study.* A. de Lucas, J.L. Valverde, P. Sánchez, F. Dorado, M.J. Ramos, J. Otero, J. Otero, J.M. Sánchez, E. Ruiz, D. Sillero, M.R. Sun Kou, M.A. Keane. December 2001-December 2004.

- Project founded by the Spanish government (CTQ2004-07350-C02-01/PQ). *New methodologies and technologies for the selective catalytic reduction of NO_x..* J.L. Valverde, A. de Lucas, P. Sánchez, F. Dorado, I. Asencio, A. Romero, P. García, A. Garrido, M.A. Keane, M.R. Sun, C. Comninellis, J. Otero, E. Ruiz, C.A. Maffiotte. December 2004- December 2007.



Facilities now existing in the catalysis lab

1.6. SELECTED JOURNAL PUBLICATIONS (1999-2005)

- Synthesis and Characterization of PILC's with Single and Mixed Oxide Pillars Prepared from two Different Bentonites. A Comparative Study. P. Cañizares, J.L. Valverde, M.R. Sun Kou, C.B. Molina, *Microporous and Mesoporous Materials,* 29, 267-281 (1999).
- Partial Oxidation of Methane to Formaldehyde over W/SiO2 catalysts. A. de Lucas, J.L. Valverde, P. Cañizares, L. Rodríguez, *Appl. Catal. A,* 184(1), 143-152 (1999).
- A Grafted Methane Partial Oxidation Catalyst from MoO2(acac)2 and HZSM-5. A. Antiñolo, P. Cañizares, F. Carrillo-Hermosilla, J. Fernández-Baeza, F.J. Fúnez, A. de Lucas, A. Otero, L. Rodríguez, J.L. Valverde, *Appl. Catal. A,* 193(1-2), 139-146 (1999).
- Enhanced Thermal Stability of Al-Pillared Smectites Modified with Ce and La. J.L. Valverde, P. Cañizares, M.R. Sun Kou, C.B. Molina, *Clays and Clay Miner.,* 48(4), 424-432 (2000).
- Partial Oxidation of Methane to Formaldehyde over Mo/HZSM-5 catalysts. A. de Lucas, J.L. Valverde, L. Rodríguez, P. Sánchez, M.T. García, *Appl. Catal. A.,* 203, 81-90 (2000).

- Modified W/HZSM-5 Catalysts: Structure and Catalytic Properties. A. de Lucas, J.L. Valverde, L. Rodríguez, P. Sánchez, M.T. García, *J. Mol. Catal. A,* 171(1-2), 195-203 (2001).
- Influence of the Synthesis Conditions on the Preparation of Titanium Pillared Clays using Hydrolysed Titanium Ethoxide as the Pillaring Agent. J.L. Valverde, P. Sánchez, F. Dorado, C.B. Molina, A. Romero, *Microporous and Mesoporous Materials,* 54(1-2), 155-165 (2002).
- Carbon-Chlorine and Carbon-Bromine Bond Cleveage in the Catalytic Hydrodehalogenation of Halogenated Aromatics. C. Menini, C. Park, J.L. Valverde, M.A. Keane, *J. Catal.,* 211, 451-463 (2002).
- Preparation and Characterization of Titanium Pillared Clays using Titanium Alkoxides: Influence of the Synthesis Parameters. J.L. Valverde, P. Sánchez, F. Dorado, I. Asencio, A. Romero, *Clays and Clay Miner.,* 51(1), 41-51 (2003).
- Cation Exchanged and Impregnated Ti-Pillared Clays for Selective Catalytic Reduction of NOx by Propylene. J.L. Valverde, A. de Lucas, P. Sánchez, F. Dorado, A. Romero, *Appl. Catal. B,* 43(1), 43-56 (2003).
- Characterization and catalytic properties of Ti-PILCs prepared at laboratory and pilot scale: a comparative study. J.L. Valverde, A. de Lucas, F. Dorado, R. Sun, P. Sánchez, I. Asencio, A. Garrido, A. Romero, *Ind. Eng. Chem. Res.,* 42, 2783-2790 (2003).
- Synthesis and characterization of Cu-Ti-PILCs for SCR of NO by propylene in presence of oxygen and H2O. Influence of calcination temperature, the copper content and the cation promoter (Ce/Ag). . J.L. Valverde, F. Dorado, P. Sánchez, I. Asencio, A. Romero, *Ind. Eng. Chem. Res.,* 42, 3871-3880 (2003).
- Influence of the Binder in the n-Octane Hydroisomerization over Palladium containing zeolite catalysts. A. De Lucas, J.L. Valverde, P. Sánchez, F. Dorado, M.J. Ramos, *Ind. Eng. Chem. Res.*, 43, 8217-8225 (2004).
- Influence of the Ion Exchanged metal (Cu, Co, Ni and Mn) on the Selective Catalytic Reduction of NOx over Mordenite and ZSM-5. A. De Lucas, J.L. Valverde, F. Dorado, A. Romero, I. Asencio, *J. Mol. Catal. A*, 225(1), 47-58 (2005).
- Hydroisomerization of n-octane over platinum catalysts with or without binder. A. De Lucas, J.L. Valverde, P. Sánchez, F. Dorado, M.J. Ramos, *App. Catal. A*, 282, 15-24 (2005).
- Study by In Situ FTIR of the SCR of NO by Propene on Cu2+-Ion Exchanged Ti-PILC, J.L. Valverde, A. de Lucas, F. Dorado, P.B. García, A. Romero, *J. Mol. Catal. A*, 230, 23-28 (2005).
- Preparation and Characterization of Fe-PILCs. Influence of the Synthesis Parameters. J.L. Valverde, A. Romero, R. Romero, P.B. García, M.L. Sánchez, I. Asencio, *Clays and Clay Miner.,* in press (2005).
- Growth of Carbon Nanofibers from Ni/Y Zeolite Based Catalysts: Effects of Ni Introduction Method, Reaction Temperature and Reaction Gas Composition. A. de Lucas, A. Garrido, P. Sánchez, A. Romero, J.L. Valverde, *Ind. Eng. Chem. Res,* in press (2005).
- Effect of the metal loading in the hydroisomerization of n-octane over beta agglomerated zeolite based catalysts. A. De Lucas, P. Sánchez, F. Dorado, M.J. Ramos, J.L. Valverde, *App. Catal. A*, in press (2005).

1.7. RESEARCH TESHES (COMPLETED DURING THE PERIOD 1998-2004).

- Luis Rodríguez (1998), *Activation of light n-alkanes by using zeolite-based catalysts.*
- Carmen Belén Molina (2001), *Synthesis and characterization of pillared clays and their further use as SCR of NO_x catalysts.*
- Isaac Asencio (2002), *SCR of NO_x by using ion exchanged zeolite-based catalysts*.
- Amaya Romero (2003), *SCR of NO_x by using Cu-ion exchanged Ti-PILCs-based-based catalysts*.

At the present, there are four on-going theses.

1.8. PARTNERS, COMPANIES AND INSTITUTIONS.

- European Union
- Ministry of Science and Technology
- Regional Council of Science and Technology (Region of Castilla-La Mancha)
- University of Castilla-La Mancha
- REPSOL-YPF
- UNIÓN FENOSA
- IBERDROLA
- CIEMAT
- University of Kentucky (USA)
- University of Utrecht (Netherlands)
- Federal Polytechnic School of Laussane (Switzerland)