Altamira Instruments

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Applications & Testing of Celero the Multi-Channel Fixed Bed Reactor for High Throughput Catalyst Screening

The AMI-200 Catalyst Characterization Instrument doubles as a reactor for study of fuel cells catalysts

Catalyst Screening in the Celero, by George Marcelin, Ph.D.

Combinatorial chemistry, a method by which chemical reactants are quickly screened for a desired product or a particular kind of activity, has been extensively used in the area of drug discovery for a number of years. The technique has been successfully extended into the areas of fine chemicals and homogeneous catalysis. However, only limited examples exist using combinatorial techniques for the discovery of solid materials.

Particularly difficult is the application of such combinatorial techniques to heterogeneous catalysts. To evaluate the performance of a catalyst one must look at a specific reaction and determine both the activity of the catalyst for the conversion of reactant(s), as well as the product distribution. In addition, we are seldom interested in initial conditions, but rather conditions after the catalyst has reached some sort of steady-state. Add to that the fact that most reactions of commercial interest are conducted at elevated pressures and it explains why so few examples exist using combinatorial techniques for discovering a heterogeneous catalyst. In reality the difficulties lie in the screening of the catalysts at somewhat realistic conditions.

One of the reasons for this slow progress has been the lack of automated instrumentation suitable for high throughput screening (HTS) of the catalysts. The small liquid-phase reactors used with homogeneous systems are not useful with heterogeneous catalysts and companies have been slow to develop their own technology. Altamira Instruments is now manufacturing the Celero, a state-of-the-art, multichannel fixed bed reactor for use in HTS applications of heterogeneous catalysts. Each CELERO module houses eight microreactors, i.e., channels or wells, operating in parallel. It was developed as a tool by Symyx Technologies for their in-house combinatorial catalysis research and has been exclusively licensed to Altamira Instruments for manufacturing and distribution.

Figure 1 shows the main components of a CELERO reactor module. A solid reactor-block houses eight radially-located wells into which reactor inserts are placed. The well volume can range between 0.5 to 10 mL allowing for catalyst weights between 0.05 and 1 gram. The eight wells are sealed with a single closure cap. Inlet and outlet connections are permanent and are located at the bottom of the reactor module thereby simplifying catalyst loading.

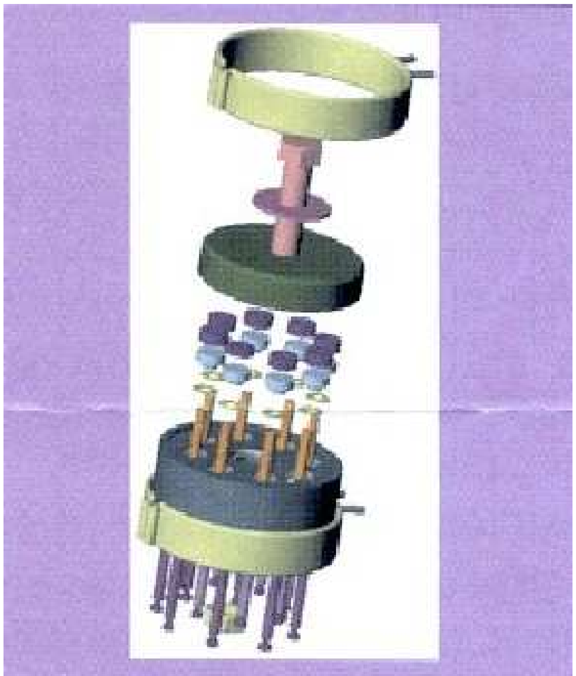

Figure 1 – Schematic of the CELERO module

The core of the reactor is heated using a series of external band heaters thus assuring even temperature distribution, typically up to 600"C. A capillary-based, flow-splitting arrangement (not shown in the figure) is used to evenly distribute the incoming feed.

Control of the CELERO system based on a single PC in combination with other embedded controllers for pneumatics and temperature control. Symyx's Impressionist ™ platform is used as the control software. Impressionist allows for the creation and editing of control routines. These routines may include defining and configuring the specific components (i.e., resources) of the reactor system, creating and modifying experimental actions, scheduling and timing experimental execution, monitoring of experiment execution via a text log-file, single-step execution control for debugging, and online help. Once defined, experiment execution is fully automated.

In a complete HTS reactor system one or more of the CELERO modules are integrated with other components as directed by the customer. A typical reactor may include, in addition to the CELERO module, a gas feed module, a liquid feed module, vaporizer, back pressure control, on-stream sampling valve, and an analytical system. The general specifications for the CELERO HTS reaction system are found in Table 1.

SOME TYPICAL TEST DATA

The unique radial design of the CELERO assures even heat distribution with minimal temperature gradients. The use of pressure-drop

Table 1. General Specification for Celero™ Reactor

Features	Basic	Custom
Number of Reactors	8 per module	Multiple modules of 8 reactors ea
Reactor Well Volume	0.5 to 7 mL	As specified
Catalyst Weight	0.05 to 1 Gram	As specified
Reactor Material	Stainless steel	Hastelloy, nitrided titanium
Maximum Reactor Temp.	600°C	Higher temperatures possible
Maximum Oven Temp.	200°C	200°C
Maximum Reactor Press.	Ambient	Up to 200 bar
Reactant Feed	Single input, gaseous	Up to 5 gases and 2 liquids
Flow Rates	Up to 50 Sccm per well	As specified
Output Sampling	Sequential	Parallel
Analysis	Valve to GC	GC with software trigger

(Covered by U.S. Patent No. 6,149,882. Use of this instrument may also be covered by one or more of the following U.S. patents: 5,985,356 and 6,004617. Additional U.S. and foreign patents pending.)

capillaries also ensures even feed distribution among the reactor wells. In a series of test experiments using a 10-channel, 7 mL/channel module, the reactor block was heated from ambient temperature to 300°C at a rate of 10°C/minute and a total nitrogen flow of 3 L/min. The individual channel temperatures, after equilibration, are shown in Table 2. Final temperatures varied by less than 1°C.

Table 2. Temperature distribution in 10-well reactor

Channel No.	1	2	3	4	5	6	7	8	9	10
Temp.(°C)	300.5	300.7	301.0	300.9	300.7	300.3	301.0	300.3	300.3	301.0

The gas and liquid flow distributions were tested using a worst-case scenario, mainly by loading only one channel with ca. 650 mg of fine alumina powder and flowing nitrogen or distilled water at various flow rates and pressures through all the channels. This test was designed in order to show that flows would not be affected by catalyst volumes and packing procedure. Figure 2 shows typical liquid feed and gas feed flow distributions. Variations from average were less that 2%.

In addition to temperature and feed flow, other factors such as channeling of the feed, may affect reactor results. Thus, an important test that any HTS system must pass is reproducibility during a real reaction using the same catalyst in all channels. Such a test was conducted in a reactor system designed around 6 CELERO modules, i.e., a total of 48-reactors wells. The reaction used as a test was the isomerization of n-hexane. The reaction was conducted at 260°C, 25 psig and the following feed flow rates: hexane (l) = 0.4 mL/min; hydrogen = 200 mL/min; helium = 100 mL/min. The reaction was allowed to proceed to steady state and the products were analyzed by gas chromatography. Figure 3 shows the overall n-hexane conversion for the 48 individual channels. All reactor wells in modules 1 and 6 exhibited reproducible results. Modules 2, 3, 4, and 5 each had one well which showed conversion results beyond the expected variation. These variations were attributed to slight temperature and flow gradients within these individual wells and were ultimately corrected. The selectivities for the main reaction products from module 1 are shown in Figure 4. Only module 1 is shown since in that module conversions were shown to vary by less than 2%. Again, the resulting selectivities were found to be in excellent agreement.

A more significant test of the CELERO HTS reactor was conducted by screening a series of mixed metal oxide catalysts for the oxidative dehydrogenation of ethane to ethylene. The series consisted of different compositions of the ternary mixed metal oxide Mo-V-Nb-O. This ternary system has been well studied and a compositional optimum has been determined to lie around Mo0.72V0.26Nb0.02Ox. For the purpose of this work, 20 different compositions were evaluated in the range of: Mo = 66-79%; V =

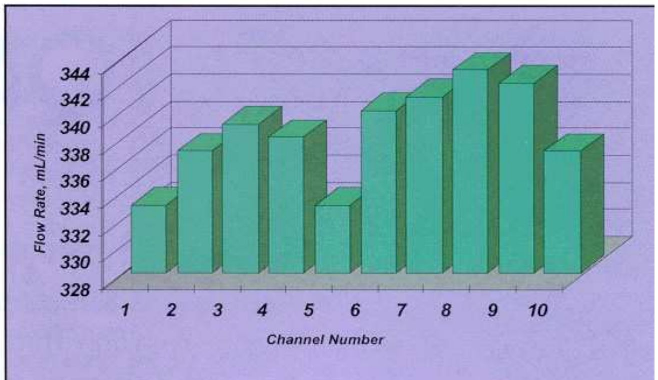

Figure 2A – Gas flow variation during test run

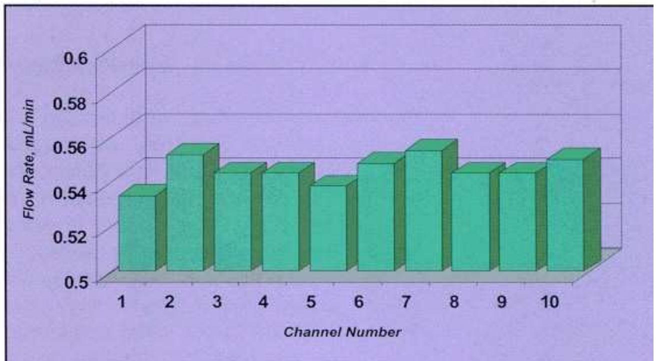

Figure 2B – Liquid flow variation during test run

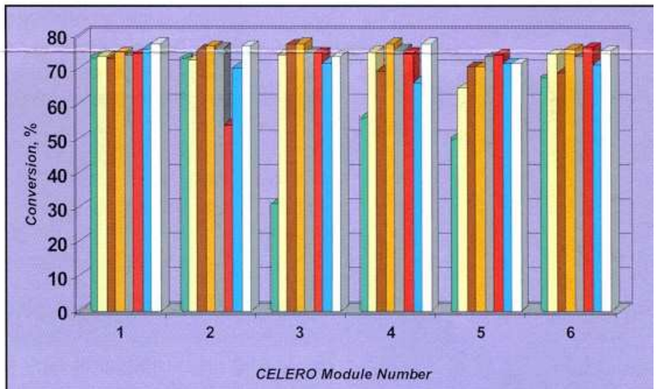

Figure 3 – Reproducibility test. N-hexane conversion

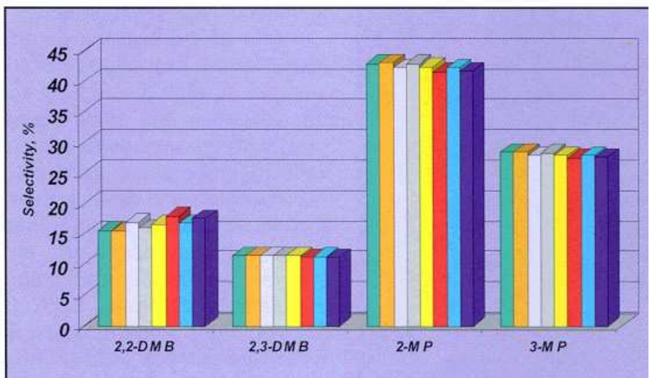

Figure 4 – Reproducibility test. Selectivites.

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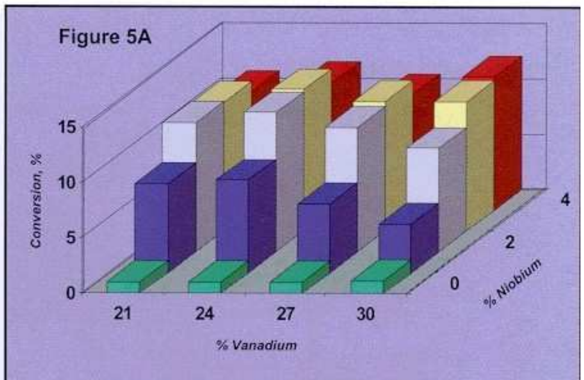
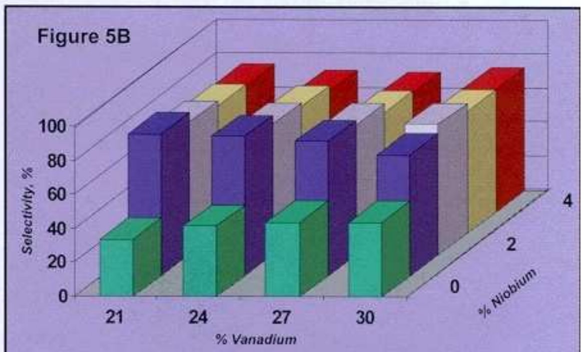
21-30%; and Nb = 0-4%. Figure 5 shows the conversion and selectivity results obtained for the twenty catalysts.

Clearly, absence of Nb results in a catalyst with little useful activity, while excessive Nb tends to reduce the selectivity to ethylene. Catalysts containing only 1% Nb exhibited the best selectivity albeit with low activity. The optimum catalysts in terms of both activity and selectivity were found in the range of Mo = 71-77%; V = 21 - 24%; and Nb = 2-3%. Indeed the best two catalysts in terms of ethylene yield were determined to be $Mo_{0.74}V_{0.24}Nb_{0.02}O_x$ and $Mo_{0.73}V_{0.24}Nb_{0.03}O_x$, very close in composition to the literature best: $Mo_{0.72}V_{0.26}Nb_{0.02}O_x$.

The development of commercial reactors for the high throughput screening of catalysts is bound to lead to increased efforts by the chemical industry to apply combinatorial chemistry techniques to the discovery of new catalysts and catalytic processes. Such a reactor must be able to use small amounts of catalysts, perform reproducibly, and operate automatically. The CELERO reactor clearly meets these requirements.



Conversions of M.M.O. Catalysts



Selectivities of M.M.O. Catalysts