ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

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HIGH THROUGHPUT SCREENING FOR THE DISCOVERY OF MORE EFFICIENT CATALYSTS FOR EMISSIONS CONTROL

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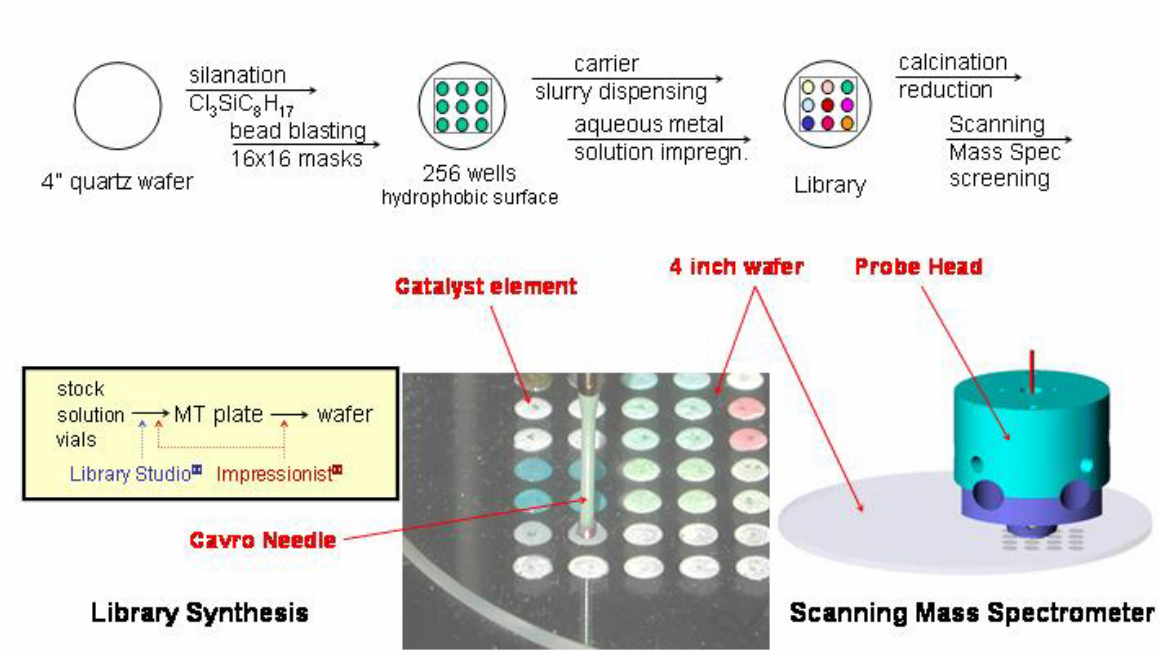
High-throughput synthesis and screening methods have been developed for the discovery of highly active catalysts used in the control of emissions from stationary and mobile sources. We have initiated a broad screening program, encompassing mixed metal oxides, perovskites as well as supported base and noble metals, for a diverse set of emissions applications in a high-throughput scanning mass spectrometer reactor [1-6]. These applications include low temperature CO oxidation for cold start automotive emissions control; Selective Catalytic Reduction (SCR) and Selective Catalytic Decomposition (SCD, direct decomposition)-DeNOx for heavy duty diesel engine tailpipe DeNOx as well as SCR-stack-$DeNO_x$ in power plant exhaust gas streams; CO_x methanation as an alternative to preferential oxidation for CO clean up, *e.g*. for the production of hydrogen in fuel processors; and Volatile Organic Compound (VOC) decomposition. The aim of this work was to discover novel compositions with significantly enhanced efficiency, provide an activity ranking of catalyst compositions and to identify general reactivity trends.

Wafer-formatted catalyst libraries were designed and synthesized *in situ* using Symyx' proprietary Library Studio® and Impressionist® software[7]. Commercial 3 or 4 inch round quartz wafers were cleaned, silanized and bead blasted through masks to produce 11x11 or 16x16 arrays of wells. These wells were then optionally pre-coated with a porous carrier layer (commercial SiO_2, Al_2O_3, TiO_2, ZrO_2 powders) using a slurry dispensing technique, dried, impregnated with metal precursor solutions using liquid dispensing robots, calcined and optionally reduced. External standards (a commercial catalyst benchmark) were dispensed onto the wafers and internal standards were

synthesized into several first row and last column wells. The remaining spots in the first row/last column were left blank to correct for the background signal during data processing (Fig. 1).

Figure 1

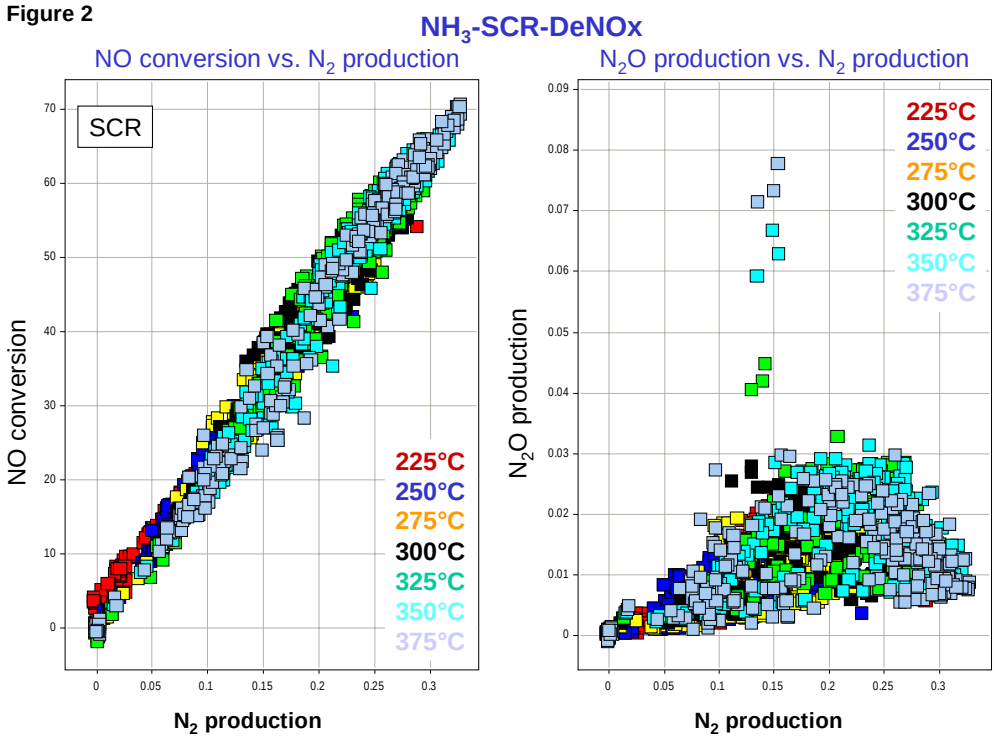


The scanning mass spectrometer[1] is a rapid primary screening tool that uses flat wafer catalyst surfaces, a scanning/sniffing nozzle and a mass spectrometer to compare relative catalytic activities. Quartz wafers are mounted on a standard wafer holder, which provides movement in the XY plane. The nozzle moves in the Z direction and is designed to isolate each independent catalyst element, deliver the feed gas and transmit a sample of the product gas stream to a quadrupole mass spectrometer (Fig. 1). Each element is heated locally from the back of the wafer using a CO_2 laser, allowing for temperatures up to 600°C. The probe head and all transfer line temperatures were kept at 200°C for these experiments. The reaction chamber was pressurized to 30 psi with Ar. Time on stream per catalyst element was approximately 3-5 minutes, and product signals for each library element were calculated as the average over the last minute of testing. Heat and mass transfer effects are negligible due to the small sample amount (less than 1mg per well). The feeds consisted of the reactants (from premixed and certified gas tanks) with Kr as internal standard in Ar carrier gas.

The raw data for each mass were first normalized to the Kr. Next, the signals of the standards and all blank elements were averaged and the conversion percentages for reactants computed, using the average from the blank wells to estimate the feed signal for each library element. The data analysis procedure is based on mass balance plots

by plotting the reactant conversion versus the product yield (uncalibrated but Kr-normalized mass spectrometer signals) as shown in Fig. 2.

Figure 2



For low temperature CO oxidation for cold start automotive emissions control, a realistic cold start feed of CO/O_2 in the presence of NO and H_2O co-feed was used. On-chip perovskite synthesis as well as methods for slurry dispensing of preformed perovskite powders onto wafers were developed. Characterization was by XRD. Perovskite catalysts allow for significant noble metal savings. Light off curves for 256 catalysts were mapped out using 10K temperature increments over 2 days.

For ammonia SCR-stack-$DeNO_x$, prior art V_2O_5-WO_3-TiO_2 for medium temperature SCR at 300C was reproduced and improved (Fig. 2). A new material for low temperature SCR has been discovered that is highly active at temperatures as low as 190C.

For methanation (hydrogenation) of mixed CO and CO_2 feeds, the methanation activity ranking of noble metals was found to be Ru>Rh>Pt>Re~Ir~Pd and for base metals by Ni>Co>Fe. CO methanation was found to be preferred over CO_2 methanation.

For VOC removal, transition metal binaries and Co-containing ternaries were screened and CoCr-based compositions identified as highly active for total hydrocarbon combustion.

In summary, Symyx' integrated primary synthesis and screening workflow has been demonstrated to be applicable to emissions control catalysis. High conversions can be achieved in Scanning Mass Spectrometer, despite the flat catalyst layer, small sample

amount, and flow over reactor geometry. This greatly minimizes any catalyst scalability risk.

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