High-Throughput Screening of Heterogeneous Catalysts for the Oxidation of Ethane to Acetic Acid in a Massively Parallel Microfluidic Reactor

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Introduction
Ethane oxidation is becoming an increasingly attractive route to acetic acid due to the availability of low cost ethane feedstock from natural gas sources [1]. The MoVNbPd mixed oxide system is among the best-performing catalysts known for this reaction [2-4]. However, a direct oxidation of ethane to acetic acid has not yet been commercialized, primarily because existing catalysts suffer from relatively low activity and/or selectivity. Thus, there remains a need for the discovery of novel catalyst systems to make this reaction commercially viable. We have applied our massively parallel microfluidic screening reactor technology, high-throughput synthesis workflow and catalyst library archive to this problem, screening more than 10,000 catalysts in a two-week period. This resulted in the generation of new lead materials and a confirmation of published results.

Results and Discussion
Catalysts were synthesized in 16x16 arrays on 3-inch quartz wafers using Symyx Library Studio® and Impressionist® software [5]. The premixed metal precursor solutions were dispensed onto the wafers using automated liquid-handling robots and the catalysts finished by subsequent drying and calcination steps. High throughput screening of the catalyst libraries was performed using a fully parallel 256-channel reactor based on a microfluidic flow distribution device and colorimetric detection methodology [6]. Acetic acid was detected using Methyl Red as the pH indicator [7].

Approximately forty catalyst libraries consisting of binary, ternary, and quaternary compositions were screened. Primary screening was initially targeted to identify the best binary combinations of redox metals selected from V, Mo, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ag, Re, Sn, Sb, Te, and Bi. The best hits and synergistic combinations of redox metal binaries were then extended to ternaries by adding single dopants selected from the main group metals, transition metals, and rare earth metals. Focused ternaries for the best hits were screened next in order to determine the most active compositional regions. Finally, the most active focus ternaries were doped with noble metals evenly over the ternary gradients. The effect of noble metal content was studied by synthesizing identical daughter wafers of the particular mixed oxide ternary followed by impregnation with solutions of different noble metal concentrations.

Patented catalyst examples were successfully confirmed in the parallel microreactor, demonstrating the relevance of the primary screen for this oxidation. The performance
ranking of redox binaries was found to be MoV >> CrV, MnV, CoV, VTi, MoTi, CoCr, and MnCr. For MoV, the Mo-rich composition gives a higher yield. The ranking of MoVX ternaries is MoV-Nb, MoV-M1, MoV-M2, MoV-M3 > MoV-Ni, MoV-Sb, MoV-Ce > MoV-Fe. Three new dopants (M1, M2, M3) were discovered that at least equal the MoVNb system under the testing conditions. Pd doping of MoVNb greatly enhances the acetic acid yield in full agreement with the published data.

Figure 1. Screening protocol showing library designs (top) and post reaction images of detection wafers (bottom). (a) Binaries of redox active metals, (b) extension of binaries into ternaries by adding dopants, (c) focus ternaries of best hits, (d) noble metal doping of MoVNb ternary. Compositional details will be given in the presentation.

References