Combinatorial discovery of oxidative dehydrogenation catalysts within the Mo-V-Nb-O system

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ABSTRACT Combinatorial methodologies were used for the synthesis and screening of mixed metal oxide heterogeneous catalysts. Primary screening at low reactant conversions at a throughput of greater than 10,000 catalyst compositions per month was performed by using simultaneous MS and photothermal deflection spectroscopy on spatially separated thick film catalysts with ~200 µg per catalyst prepared by using automated liquid dispensing. Secondary screening under realistic operating conditions was performed at a throughput of greater than 3,000 catalyst compositions per month on ~50 mg of catalyst in an array of fixed bed microreactors with gas chromatograph detection. The approach was validated by the discovery of catalysts with superior performance to those previously described for the oxidative dehydrogenation of ethane to ethylene. We show the full implementation and integration of combinatorial methodologies for synthesis, screening, discovery, and optimization of multicomponent heterogeneous catalysts.

Although combinatorial methodologies are practiced routinely for drug discovery (1, 2), this general approach is compelling in other fields where predictive abilities also are restricted. Recently, combinatorial methods have been applied within several different areas of materials science, where increasing compositional or structural complexity often results in unique or otherwise improved properties (1-12). Structural and compositional complexity may result in systems consisting of several components functioning cooperatively. In these combinations, the synergy of the multicomponent system results in performance characteristics that are particularly difficult to predict a priori. Presently, the vast majority of complex inorganic solids and multicomponent materials remain unexplored (13), in part because composition-structure-property relationships for such systems are limited. The utility of combinatorial chemistry, i.e., the ability both to prepare and to screen vast numbers of compounds in a rapid fashion, may be most productively realized within such systems. Here, we describe an integrated combinatorial program that has resulted in the discovery of improved multicomponent heterogeneous catalysts for the oxidative dehydrogenation of ethane to ethylene. Bringing combinatorial methodologies to bear on this application is particularly appealing because catalysis discovery has relied traditionally on an iterative trial-and-error synthesis and characterization strategy that is both tedious and time consuming.

The parallel synthesis of catalytic materials by the use of automation and miniaturization techniques is most efficient when preparing very small quantities (~1 mg) of catalysts. The characterization of such small amounts of catalytic materials frequently is hindered by the lack of sensitive high throughput screening methodologies, particularly for reactions of low probability such as the partial oxidation of hydrocarbons. These obstacles have been overcome in our laboratories, and an integrated combinatorial discovery program for heterogeneous catalysis has been realized. We have reported previously the preliminary implementation of such a program for CO oxidation and NO reduction by noble metals and copper (12). Here, we describe the full implementation for the oxidative dehydrogenation of ethane to ethylene, which is far more challenging from the perspective of catalyst screening caused by a lower rate of reaction and the presence of undesirable side reactions. In addition to MS, an optical detection scheme for ethylene has been developed as part of the primary screen, along with a parallel fixed bed microreactor as the secondary screen.

The development of efficient heterogeneous catalysts for the gas phase oxidative dehydrogenation of light paraffins is of particular interest because of the economic benefits of using light paraffins for the production of important base chemicals (14-18). The low-temperature oxidative dehydrogenation of C\textsubscript{2}H\textsubscript{6} to C\textsubscript{2}H\textsubscript{4} has been a research topic of consistent interest after the report of catalytic activity in the Mo-V-Nb-O system below 300°C in 1978 (18-22). In the work reported here using combinatorial methodologies for catalyst synthesis and screening, we demonstrate our ability both to reproduce the results in the Mo-V-Nb-O and related systems, as they have been described previously in the literature, and to identify similar but improved catalysts.

The utility of combinatorial methods applied to heterogeneous catalysis depends ultimately on the ability to prepare bulk-like materials in a high throughput manner (23). If trends measured in a combinatorial library are to correlate with bulk trends, then the identity of catalytically active sites should be the same in the two cases, assuming the reaction mechanisms do not change from low conversions as measured in the primary, high throughput screen to much higher conversions in secondary and tertiary screens. The purpose of the high throughput screen is the rapid screening of many catalysts to eliminate compositions from further examination, which allows the accelerated study of large regions of composition space with the intent of extracting relative trends that suggest continued study using focused primary screens and secondary screens.

The general strategy applied in our labs for rapid primary screening involves the creation of arrays of thick films that are spatially separated catalyst libraries of 100-200 µg per catalyst. Typically, ~150 catalyst compositions are measured per experiment in the primary screen. These catalyst films are prepared from stabilized sol-gel precursors by automated solution deposition techniques (24).

Metal alkoxide solutions (0.5 M) were prepared by refluxing commercially available metal alkoxides in 2-methoxyethanol

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PNAS is available online at www.pnas.org.

This paper was submitted directly (Track II) to the Proceedings office. Abbreviation: PTD, photothermal deflection.

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acted gas mixture are carried through a capillary to the
onal directions within the reaction chamber. A stationary
arrays are loaded into a system containing a reaction chamber.
quantities of catalyst.
for which reliable data are collected under realistic
operating conditions. Particularly interesting catalyst compo-
sitions may continue to be examined at a tertiary screen level,
or examined in a secondary screen. Typically, areas of high product yield may be re-examined in the primary screen or examined in a secondary screen. Typically, ~50 catalyst compositions (25–50 mg) are examined per experiment in the secondary screen by using parallel fixed bed microreactors. Current operating conditions in the secondary screen allow for a total throughput of more than 3,000 catalyst compositions per month for which trends are observed under conditions of low reactant conversions. Areas of high product yield may be re-examined in the primary screen or examined in a secondary screen. Typically, ~50 catalyst compositions (25–50 mg) are examined per experiment in the secondary screen by using parallel fixed bed microreactors. Current operating conditions in the secondary screen allow for a total throughput of more than 3,000 catalyst compositions per month for which reliable data are collected under realistic operating conditions. Particularly interesting catalyst compositions may continue to be examined at a tertiary screen level, i.e., studies of the effects of reaction temperature, flow rate, and feed composition, using bench-scale reactors with gram quantities of catalyst.

For purposes of primary catalytic screening, combinatorial arrays are loaded into a system containing a reaction chamber and an analysis chamber, see Fig. 1 (12, 25, 26). The library is placed onto a platform capable of translation in three orthogonal directions within the reaction chamber. A stationary nozzle allows the reaction gas to be delivered onto each catalyst independently, and the resulting products and unre-
acted gas mixture are carried through a capillary to the detection system in the analysis chamber. The temperature of a single element is controlled by using a CO2 laser for heating, a remote temperature sensor, and a feedback control loop. The composition of the product gas is measured once the gas flow, temperature, and pressure have stabilized. Single-element heating and local exposure of reactant gases prevent premature aging of catalyst elements before measurement and eliminate all contributions from neighboring catalysts.

Catalytic screening in the analysis chamber was performed by using both a mass spectrometer equipped with an electron impact (EI) ionizer and a photothermal deflection (PTD) detector. While EI-MS offers a universal scheme for detecting most molecules, it cannot measure the C2H4 concentration at the ppm level in the presence of high concentrations of C2H6 because the ion fragmentation pattern of C2H4 is a subset of that of C2H6. This serious problem has been solved by PTD, which relies on selective IR laser excitation of C2H4 and offers a very high discrimination factor against C2H6 (on the order of 106) and other species that are present in the product stream and are detected with EI-MS, such as CO2, CO, and H2O (27, 28). In the experimental setup, a CO2 laser, operated at a single line (10P14) to be in resonance with the ν7 mode (949.48 cm−1) of C2H4, is used as the pump laser, and a 10-mW HeNe laser is used as the probe laser. The sensitivity of the PTD detector for C2H4 is below 0.1 ppm. The product gas is introduced into both the PTD detector and the ioniza-
tion zone of the mass spectrometer through a split capillary, and oxidation products C2H4 and CO2 (apart from H2O) were found. The presence of CO is masked by N2. Approximate reaction selectivities at low conversions thus are determined through the measurement of both the desired product, C2H4, and the undesired combustion side product, CO2.

Library samples were loaded into the reaction chamber and screened by PTD and MS at temperatures between 300 and 400°C. The reactant gas was a mixture of N2, C2H4, and O2 in a molar ratio of 5:4:1. The reaction chamber pressure was maintained at ~760 Torr. After the flow and pressure were stabilized, each catalyst was heated sequentially to the reaction temperature by using a CO2 laser, and product formation was measured for 60–90 sec. Initially, a library containing multiple quantities of a single catalyst composition known to be active for C2H4 production was measured between 300°C and 400°C. The optimal reaction temperature and catalyst mass (solution
becomes more difficult in this high throughput, primary
differentiate between the performance of library elements
distinction between library elements decreases, the ability to
biom in 3% increments in Fig. 2
55–85% molybdenum, 15–45% vanadium, and 0–30% nio-
duction at 400°C for libraries of (resulting in 10% compositional increments per matrix ele-
rotation operation.

Focus libraries included 50–100% molybdenum and 0–50%
were prepared to focus on the most active area, see Fig. 2.

For greater compositional precision, additional libraries
were prepared to focus on the most active area, see Fig. 2.
Focus libraries included 50–100% molybdenum and 0–50%
avanadium and niobium in 5% increments in Fig. 2a, and
55–85% molybdenum, 15–45% vanadium, and 0–30% nio-
bium in 3% increments in Fig. 2b. As the compositional
distinction between library elements decreases, the ability to
differentiate between the performance of library elements
becomes more difficult in this high throughput, primary
graphs, each containing three identical channels, CO, CO2,
and C2H6 were separated in 3 min. In an initial examination in which the concentration of niobium was varied
between 3% and 12%, compositions of maximum C2H6 con-
version and C2H4 selectivity were found to decrease with
increasing niobium concentration with maxima occurring
along the 3% niobium row. Subsequently, another series of
bulk samples was prepared with the niobium concentration
varying from zero to 4%.

Based on the results of Table 1, it appears that whereas the binary Mo-V catalysts will catalytically dehydrogenate C2H6 to a very limited extent, the presence of niobium dramatically increases both activity and selectivity. The addition of small amounts of Nb is most effective within the range of 1% < Nb < 4%. Based on C2H4 yield, catalysts with Nb concentrations of 2–4% are indistinguishable but are clearly better than either 1% or greater than 4% Nb. Optimal compositions of Mo and V from samples with 2% ≤ Nb ≤ 4% are within the ranges of 70% < Mo < 77% and 21% < V < 27%, whereas the most optimal composition is Mo ~ 73%, V ~ 24%, Nb = 3%, ±1%. This compositional range and optimal composition may be compared with those described by Thorsteinson et al. (18), namely, 61% < Mo < 77%, 19% < V < 31%, 4% < Nb < 9% with an optimal composition of 73% Mo, 18% V, 9% Nb. Prepared on a gram scale or a 50-mg scale, this composition measured in our system results in 6.1% conversion with 83.2% selectivity. Our microreactor results (~50 mg) are consistent with those of Thorsteinson (tens of grams) and have greater compositional specificity.

Table 1. Parallel reactor data at 300°C for oxidized Mo79-66V1-30Nb0-4

<table>
<thead>
<tr>
<th>Composition</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo79V21</td>
<td>0.51(8)</td>
<td>34(10)</td>
</tr>
<tr>
<td>Mo76V24</td>
<td>0.86(1)</td>
<td>41.8(3)</td>
</tr>
<tr>
<td>Mo73V27</td>
<td>0.99(1)</td>
<td>43.9(2)</td>
</tr>
<tr>
<td>Mo70V30</td>
<td>1.2(1)</td>
<td>44.0(3)</td>
</tr>
<tr>
<td>Mo78V21Nb1</td>
<td>8.0(1)</td>
<td>83.2(1)</td>
</tr>
<tr>
<td>Mo75V24Nb1</td>
<td>8.3(1)</td>
<td>81.9(1)</td>
</tr>
<tr>
<td>Mo72V27Nb1</td>
<td>6.2(1)</td>
<td>79.1(1)</td>
</tr>
<tr>
<td>Mo69V30Nb1</td>
<td>4.4(1)</td>
<td>71.0(1)</td>
</tr>
<tr>
<td>Mo77V21Nb2</td>
<td>11.7(1)</td>
<td>77.7(1)</td>
</tr>
<tr>
<td>Mo74V24Nb2</td>
<td>12.6(1)</td>
<td>76.7(1)</td>
</tr>
<tr>
<td>Mo71V27Nb2</td>
<td>11.3(1)</td>
<td>76.3(1)</td>
</tr>
<tr>
<td>Mo68V30Nb2</td>
<td>9.4(1)</td>
<td>76.8(2)</td>
</tr>
<tr>
<td>Mo76V21Nb3</td>
<td>11.6(1)</td>
<td>74.9(1)</td>
</tr>
<tr>
<td>Mo73V24Nb3</td>
<td>12.8(1)</td>
<td>74.4(1)</td>
</tr>
<tr>
<td>Mo70V27Nb3</td>
<td>11.8(1)</td>
<td>70.7(1)</td>
</tr>
<tr>
<td>Mo67V30Nb3</td>
<td>11.8(1)</td>
<td>71.9(1)</td>
</tr>
<tr>
<td>Mo75V21Nb4</td>
<td>10.7(1)</td>
<td>74.1(1)</td>
</tr>
<tr>
<td>Mo72V24Nb4</td>
<td>11.5(1)</td>
<td>70.9(1)</td>
</tr>
<tr>
<td>Mo69V27Nb4</td>
<td>10.5(1)</td>
<td>69.9(1)</td>
</tr>
<tr>
<td>Mo66V30Nb4</td>
<td>12.1(1)</td>
<td>72.1(1)</td>
</tr>
</tbody>
</table>

Under identical synthesis and reaction conditions, the optimal composition reported by Thorsteinson (18, 19), Mo73V18Nb9, converts 6.1(6)% at a selectivity of 83.2(9)%.
Based on literature examples (19, 29), the addition of antimony and calcium is expected to improve further the performance of the Mo-V-Nb-O system. When these additional elements are included, the divergence of the optimal catalyst composition from previously reported materials is even greater. Our results clearly show that the partial substitution of Sb for Nb improves the catalyst performance, as described previously. However, unlike the catalysts previously described in the literature, Sb-rich (compared with Nb) compositions display further improved catalytic performance. Although the replacement of Nb solely by Ca generally decreases the catalytic performance, the combination of Sb and Ca results in improved performance. Finally, the inclusion of Li improves the catalytic performance even further. Selected results are shown in Table 2 for 12 catalysts, all of which have performance characteristics that exceed the best catalysts heretofore reported in the literature. Superior performance is judged by selectivity improvements at similar conversions.

Combinatorial methodologies encompassing all synthetic and screening steps have been used to determine the optimal composition of catalysts for the oxidative dehydrogenation of C2H6 within the Mo-V-Nb-O composition space. Using primary and secondary screening techniques, the optimal composition has been determined within ±2% for all elements. The use of miniaturized, parallel fixed bed reactors on a 50-mg scale has resulted in the reproduction of literature trends using lab scale reactors on a gram scale at greater compositional resolution than that originally reported. New and improved catalytic materials were discovered in the compositional space near that previously reported. The inclusion of Sb, Ca, and Li dopants improved the catalyst even further. The feasibility of combinatorial synthesis and screening techniques has been validated for their future use in catalyst discovery and optimization programs.

### Table 2. Parallel reactor data at 300°C for oxidized Mo71V24(Nb,Sb,Ca,Li)5

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb0.5Sb2Ca2.5</td>
<td>9.8(1)</td>
<td>83.2(2)</td>
</tr>
<tr>
<td>Nb2.5Ca2.5</td>
<td>7.9(1)</td>
<td>85.7(3)</td>
</tr>
<tr>
<td>Nb0.5Sb2Ca2Li0.5</td>
<td>9.2(1)</td>
<td>84.2(4)</td>
</tr>
<tr>
<td>Nb2.5Ca2Li0.5</td>
<td>10.8(1)</td>
<td>85.5(2)</td>
</tr>
<tr>
<td>Nb0.5Sb2Ca1.5Li1</td>
<td>7.3(6)</td>
<td>86.7(6)</td>
</tr>
<tr>
<td>Nb0.5Sb2Ca1Li1.5</td>
<td>8.1(1)</td>
<td>85.8(5)</td>
</tr>
<tr>
<td>Nb0.5Sb2Li2.5</td>
<td>9.8(1)</td>
<td>87.9(1)</td>
</tr>
<tr>
<td>Nb2.5Ca0.5Li2</td>
<td>9.3(1)</td>
<td>87.6(1)</td>
</tr>
<tr>
<td>Nb0.5Sb2Li2.5</td>
<td>8.6(2)</td>
<td>87.2(3)</td>
</tr>
</tbody>
</table>