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High-throughput synthesis and screening of V–Al–Nb and Cr–Al–Nb oxide libraries for ethane oxidative dehydrogenation to ethylene

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Abstract

High-throughput synthesis and screening of mixed metal oxide libraries for ethane oxidative dehydrogenation to ethylene have been developed. A 144-member catalyst library was prepared on a 3 in. quartz wafer. An apparatus for screening catalytic activity and selectivity of a 144-member catalyst library consists of a reaction chamber, where each member can be heated individually by a CO_2 laser and reactant gases can be delivered locally to each member. The reaction products, ethylene and CO_2, are detected by photothermal deflection spectroscopy and by mass spectrometry. A 144-member catalyst library can be screened in slightly more than 2 h. V–Al–Nb oxide and Cr–Al–Nb oxide libraries are illustrated as examples. V–Al–Nb oxide catalysts are high temperature catalysts and Nb did not affect the catalytic activity of the V–Al oxides in contrast to the effect of Nb found in Mo–V–Nb oxides. However, for the Cr–Al–Nb oxide library, the most active catalyst contains about 4% Nb. These results suggest that a fine composition mapping is necessary for discovery of new heterogeneous catalysts in those ternary systems.

Keywords: V–Al–Nb oxide; Cr–Al–Nb oxide; Oxidative dehydrogenation

1. Introduction

The use of combinatorial chemistry has demonstrated great success in the pharmaceutical industry in discovering new drug candidates. With parallel synthesis and high-throughput screening technologies, a large number of compounds can be synthesized and screened in a short period of time, and, therefore, the discovery time has been shortened dramatically [1]. Now combinatorial chemistry is being applied to the discovery of new solid state materials [2–4]. Heterogeneous catalysts have played important roles in the chemical and petrochemical industries; however, the discovery of new catalysts is often achieved by conventional trial-and-error approaches, which are labor-intensive processes. The usefulness of rational design in discovery of new catalysts is limited since heterogeneous catalysis in general is a complicated and not a well understood process. Therefore, rapidly synthesizing a large number of chemically distinct materials and screening for desired properties in a chemical reaction can accelerate the discovery process significantly. Although several techniques have been developed to screen heterogeneous catalyst libraries,

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most of them are not chemically specific, such as IR thermography [5] or only one of the many possible products is detected [6].

Converting the abundant alkanes to alkenes catalytically at low temperature has been a challenge in chemical and petrochemical industry for many years. Finding proper heterogeneous catalysts is a key to the success of this process. Alkane dehydrogenation is a thermodynamically unfavorable reaction and requires high reaction temperatures to drive the equilibrium to favor the formation of alkenes. Due to the high reaction temperature and the absence of oxygen, coke formation becomes serious, and the deactivated catalysts have to be regenerated. In contrast, oxidative dehydrogenation of alkanes to alkenes is a thermodynamically favorable reaction, which can occur without coke formation on the catalyst surface. However, alkane oxidative dehydrogenation is accompanied by combustion by-products CO and CO_2. Therefore, highly active and selective catalysts at low temperature are required. One of the best known catalysts that is active at 300°C contains a mixture of molybdenum, vanadium and niobium oxides [7,8]. The complexity of ternary systems suggests that high-throughput synthesis and screening technologies will be useful for developing new catalysts. Here we report high-throughput synthesis and screening of mixed metal oxide libraries for ethane oxidative dehydrogenation to ethylene, illustrated with V–Al–Nb and Cr–Al–Nb oxide libraries.

2. Experimental details

High-throughput synthesis of mixed metal oxide library was conducted on a 3 in. diameter quartz wafer [9,10]. A mixed metal oxide library was prepared by sol–gel methods with metal alkoxides in 2-methoxyethanol as precursors. The precursor library was prepared with automatic dispensing robotics and transferred to the quartz wafer (3.0 μl solution for each member). After gelation and calcination, a chemically distinct mixed metal oxide library (144 members) containing about 1.5 μmol of material for each member is obtained on a 3 in. quartz wafer.

A specially constructed experimental apparatus [11] was used to screen catalytic activity and selectivity of the catalyst library on a 3 in. quartz wafer. The quartz wafer containing the catalyst library is loaded onto a two-dimensional screening stage underneath a probe with concentric tubing for gas delivery/removal and sampling. Only the catalyst that is being tested is exposed to the reactant gases, and the excess reactants are removed from the system by a vacuum line. A catalyst is heated by a CO_2 laser to the desired temperature before the measurement commences. No other catalyst experiences heat or the reactant gases since the heating is localized and reactant gases are delivered locally. The measurement of product as well as reactant concentrations is achieved by sampling the gas mixture directly above the catalyst and transporting it through a capillary transfer line to the detectors. Each measurement takes about 1 min to complete, and slightly more than 2 h are needed to complete a 144-member library. The reactant gas contains a mixture of C_2H_6, O_2 and Ar with a ratio of 4:1:5 in screening catalysts for ethane oxidative dehydrogenation to ethylene. Reactant gases can be switched easily to screen catalysts for other chemical reactions [9]. Two main products from ethane oxidative dehydrogenation — ethylene and CO_2 — are detected by a photothermal deflection detector and mass selective detector simultaneously. Carbon monoxide was not monitored here even though carbon monoxide was observed as a side-product in literature [12]. Ethylene and CO_2 productions from new catalysts are compared with those produced by the Mo–V–Nb oxide catalysts [7] prepared on a flat surface [10]. Although the catalyst activity is measured at low conversions, such a measurement correlates well with that measured at high conversions as demonstrated in the Mo–V–Nb oxide catalyst library [10].

3. Results and discussion

We chose to prepare V–Al–Nb oxide libraries and screen their catalytic activity and selectivity for ethane oxidative dehydrogenation to ethylene because V_2O_5/Al_2O_3 distinguishes itself from the other literature catalysts with high ethylene productivity [12]. Although the reaction temperature for V_2O_5/Al_2O_3 is high, by incorporating Nb oxide into V_2O_5/Al_2O_3 we may obtain more active and selective catalysts since niobium oxide has been reported in numerous catalytic systems to enhance metal oxide catalytic activity and selectivity in producing ethylene [7,13,14]. A library of V–Al–Nb mixed metal oxide was prepared

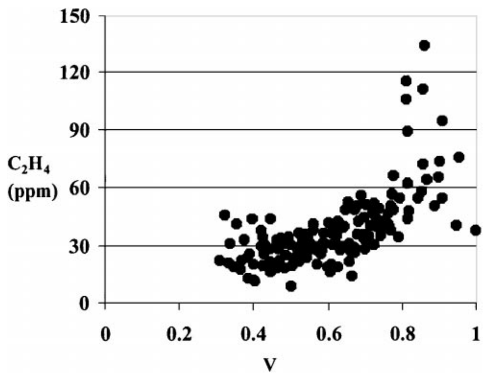

Fig. 1. Production of ethylene in ppm (at 550°C) versus V content in a V–Al–Nb oxide catalyst library. The most active catalyst contains 86% V and 14% Al.

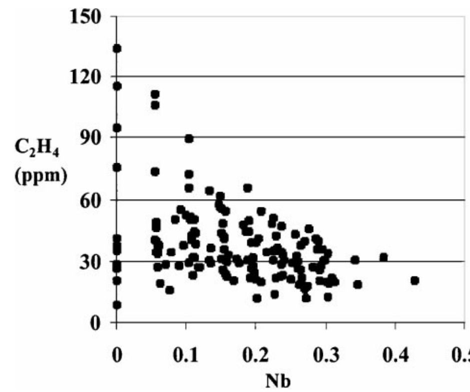

Fig. 2. Production of ethylene in ppm (at 550°C) versus Nb content in V–Al–Nb oxide catalyst library. The most active catalyst contains no Nb.

by sol–gel methods. Vanadium triisopropoxide oxide (0.50 M), aluminum triisopropoxide (0.50 M), and niobium pentaethoxide (0.50 M) in 2-methoxyethanol were used as metal oxide precursors. An automatic dispensing system was used to deliver aliquots of the above metal solutions into wells of a microtiter plate, resulting in a 16×16×16 of a 3 in. diameter quartz wafer with a 12×12 square array. To better utilize available surface area, the 16×16×16 triangular array of solutions was mapped into part of the 12×12 square array. Array members consisted of approximately 3 mm diameter droplets with adjacent droplets separated by about 1 mm. The array members were exposed to laboratory moisture at 25°C for gelation, then heated to 60°C to remove solvent, and calcined to 400°C in air. Since the stock solutions of metal precursors are 0.50 M, each member contains 1.5 μmol metal oxide.

The V–A1–Nb oxide catalyst library was then screened for catalytic activity at 400°C. Ethylene produced at 400°C is only about 20 ppm with the best catalyst containing about 86% V. This catalyst is less active than the most active member in the Mo–V–Nb oxide library prepared similarly (44 ppm ethylene produced at 400°C) [10]. When the same catalyst library was screened at 550°C as shown in Fig. 1, the signals are substantially higher. $V_{0.86}Al_{0.14}O_x$ is the most active member producing 134 ppm ethylene. However, Nb showed (Fig. 2) no obvious effect in enhancing the catalytic activity for V–Al oxide, suggesting that the synergistic effect is absent in this case [15].

Similarly, we prepared a Cr–Al–Nb oxide library and studied the effect of Nb on the catalytic activity and selectivity of Cr–Al oxides [16]. Chromium(III) 2-ethylhexanoate (0.50 M) was used as the Cr precursor. Linear gradient mapping was performed along the three directions, resulting in a 16×16×16 triangular array of metal solutions. Metal composition in the precursor solutions is listed in Table 1 as the composition of calcined catalysts. Fig. 3 and Table 1 showed the ethylene (in ppm) produced by a Cr–Al–Nb oxide library at 400°C and the catalysts' composition. The 16×16×16 triangular library was presented in a 16×16 rectangular format with blanks on the upper right corner (Fig. 3). Similar formats are presented for other libraries with com-

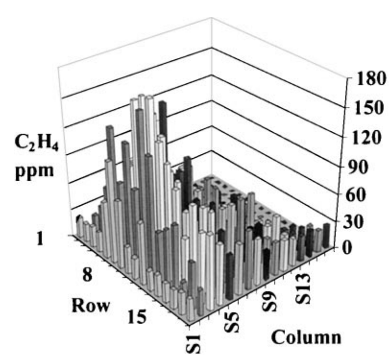

Fig. 3. Ethylene in ppm produced by a Cr–Al–Nb oxide library at 400°C. Member (row 1, column 1) contains Al_2O_3, member (16, 1) contains CrO_3 and member (16, 16) contains Nb_2O_5.

Table 1
Composition of a ternary Cr–Al–Nb oxide library and ethylene produced in ppm at 400°C for each member of the library[a]

Row	Column	Cr_x	Al_y	Nb_z	C_2H_4 (ppm) produced
1	1	0.000	1.000	0.000	21.9
2	1	0.066	0.935	0.000	20.5
2	2	0.000	0.936	0.064	25.6
3	1	0.131	0.869	0.000	23.5
3	2	0.066	0.870	0.064	41.2
3	3	0.000	0.871	0.129	23.7
4	1	0.197	0.803	0.000	22.4
4	2	0.131	0.804	0.064	67.3
4	3	0.066	0.805	0.129	23.3
4	4	0.000	0.806	0.194	22.7
5	1	0.263	0.737	0.000	61.5
5	2	0.197	0.738	0.065	134.8
5	5	0.000	0.741	0.259	25.2
6	1	0.329	0.671	0.000	109.9
6	6	0.000	0.675	0.325	24.1
7	1	0.395	0.605	0.000	73.6
7	2	0.330	0.605	0.065	128.8
7	3	0.264	0.606	0.130	167.3
7	7	0.000	0.609	0.391	25.5
8	1	0.462	0.538	0.000	29.8
8	3	0.331	0.540	0.130	175.0
8	4	0.265	0.540	0.195	153.9
8	8	0.000	0.543	0.457	24.3
9	1	0.529	0.472	0.000	23.3
9	2	0.463	0.472	0.065	169.6
9	3	0.397	0.473	0.130	177.7
9	9	0.000	0.476	0.524	25.3
10	1	0.595	0.405	0.000	67.2
10	2	0.530	0.405	0.065	130.4
10	10	0.000	0.409	0.591	24.1
11	1	0.662	0.338	0.000	21.7
11	3	0.531	0.339	0.130	123.0
11	11	0.000	0.342	0.658	24.1
12	1	0.730	0.271	0.000	23.8
12	3	0.598	0.271	0.130	103.1
12	4	0.533	0.272	0.196	75.4
12	12	0.000	0.274	0.726	27.2
13	1	0.797	0.203	0.000	21.0
13	8	0.335	0.205	0.460	63.8
13	13	0.000	0.206	0.794	19.0
14	1	0.864	0.136	0.000	20.4
14	3	0.733	0.136	0.131	98.4
14	14	0.000	0.138	0.862	23.3
15	1	0.932	0.068	0.000	24.1
15	9	0.404	0.069	0.528	54.9
15	15	0.000	0.069	0.931	24.4
16	1	1.000	0.000	0.000	24.2
16	3	0.869	0.000	0.131	80.1
16	16	0.000	0.000	1.000	26.4

[a] Compositions of the catalysts are listed as $Cr_xAl_yNb_zO_n$ (n is a number that satisfies the valence requirement of $Cr_xAl_yNb_zO_n$).

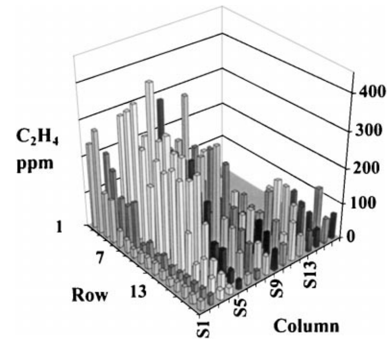

Fig. 4. Ethylene in ppm produced by a focused Cr–Al–Nb oxide library at 400°C. Member (1, 1) contains $Cr_{0.14}Al_{0.86}O_x$, member (16, 1) contains CrO_3 and member (16, 16) contains $Cr_{0.45}Nb_{0.55}O_x$.

positions of catalysts in three vertices. The catalysts with optimum ethylene production are in the region close to $Cr_{0.35}Al_{0.55}Nb_{0.10}O_x$ with an ethylene production of about 178 ppm. This catalyst is much more active than the most active member in the Mo–V–Nb oxide library (44 ppm ethylene produced) [10]. A focused library of Cr–Al–Nb oxide was then prepared with member (1, 1) containing $Cr_{0.14}Al_{0.86}O_x$, the member (16, 1) containing CrO_3, and member (16, 16) containing $Cr_{0.45}Nb_{0.55}O_x$. The most active member in this library is $Cr_{0.28}Al_{0.68}Nb_{0.04}O_x$, which produced 428 ppm ethylene (see Fig. 4). Clearly, $Cr_{0.28}Al_{0.68}Nb_{0.04}O_x$ is a much more active catalyst than either $V_{0.86}Al_{0.14}O_x$ or any Mo–V–Nb oxide catalyst for the oxidative dehydrogenation of ethane to ethylene. Fig. 5 shows CO_2 produced by the focused

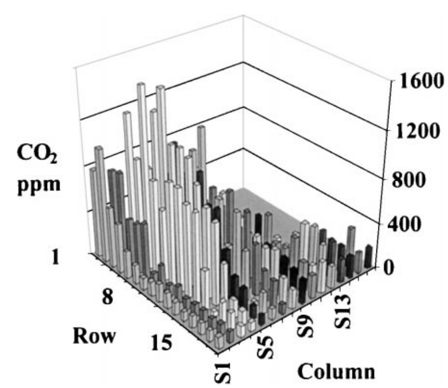

Fig. 5. CO_2 in ppm produced by the focused Cr–Al–Nb oxide library at 400°C.

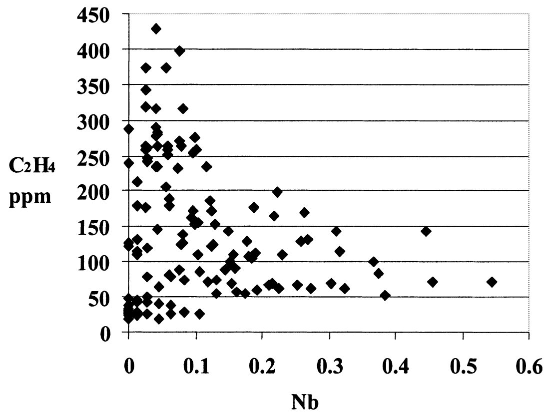

Fig. 6. Production of ethylene (in ppm) versus the Nb content of the focused Cr–Al–Nb oxide library. The most active catalyst contains about 4% Nb.

Cr–Al–Nb oxide library. Although the Cr–Al–Nb oxide library is more active than the Mo–V–Nb oxide library in producing ethylene, the ethylene selectivity of the Cr–Al–Nb oxide library (30–50%) is lower than that of the Mo–V–Nb oxide library (about 90%) [10]. More importantly, the niobium content enhances the catalysts' activity, reaching a maximum at the Nb content of about 4% (see Fig. 6).

Once an interesting catalyst is identified, its production of ethylene and CO_2 can be screened at different temperatures. In the focused Cr–Al–Nb oxide library, very active members (6, 4) and (8, 7) were screened at temperatures from 350 to 450°C. Arrhenius plots for production of ethylene and CO_2 were obtained for member (6, 4) (see Fig. 7) and member

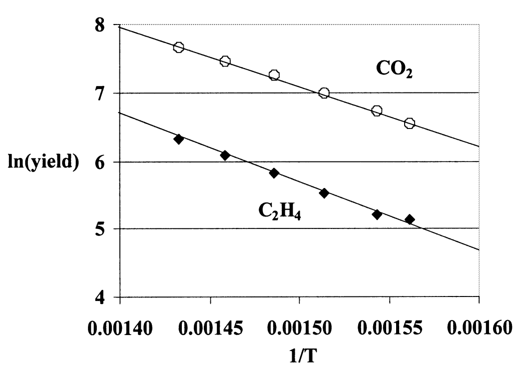

Fig. 7. Arrhenius plot of ethylene and CO_2 relative yield for member (6, 4) of the focused Cr–Al–Nb oxide library.

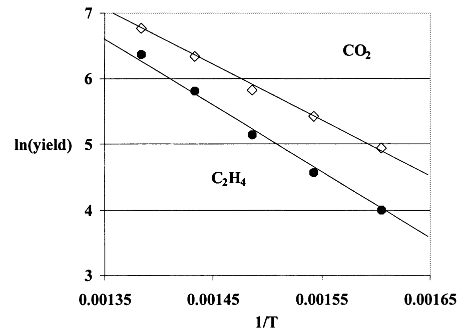

Fig. 8. Arrhenius plot of ethylene and CO_2 relative yield for member (8, 7) of the focused Cr–Al–Nb oxide library.

(8, 7) (see Fig. 8) for estimation of the activation energies for the formation of ethylene and CO_2. At low conversion, ethylene and CO_2 productions in ppm are proportional to their yield, and therefore, the rate constants for their formations. For production of ethylene, the apparent activation energies for member (6, 4) ($Cr_{0.28}Al_{0.68}Nb_{0.04}O_x$) and member (8, 7) ($Cr_{0.27}Al_{0.63}Nb_{0.10}O_x$) are 20±1 and 21±1 kcal/mol, respectively. For the combustion by-product CO_2, the apparent activation energies for member (6, 4) ($Cr_{0.28}Al_{0.68}Nb_{0.04}O_x$) and member (8, 7) ($Cr_{0.27}Al_{0.63}Nb_{0.10}O_x$) are 18±1 and 16±1 kcal/mol, respectively. The activation energies obtained on the catalyst library on a flat surface are consistent with the activation energies of Mo–V–Nb oxide catalysts obtained on large scales [14].

4. Conclusion

The high-throughput synthesis of mixed metal oxides and screening by mass selective and photothermal deflection detection systems provide a means for studying the oxidative dehydrogenation of ethane as a function of catalyst composition. Both V–Al–Nb oxide and Cr–Al–Nb oxide libraries were prepared and screened for catalytic activity and selectivity of ethane oxidative dehydrogenation to ethylene. No obvious effect of Nb has been observed in the V–Al–Nb oxide library; however, the catalytic activity reached a maximum at a content of 4% Nb in the Cr–Al–Nb library. In both cases, the most active members are limited in a narrow range of composition of the mixed metal oxide library. Therefore, high-throughput synthesis and screening of solid materials for heterogeneous catalysis have demonstrated its usefulness for discovery of new catalysts in those complex ternary systems. Although the solid materials prepared on quartz wafers are screened at low conversion, it has been demonstrated that the low conversion results can be correlated with the high conversion results [10]. To date, a large number of solid materials have been screened for ethane oxidative dehydrogenation to ethylene with many lead catalysts discovered. The lead catalysts discovered have been successfully scaled up to the 20 g scale. A detailed account of these newly discovered catalysts will be published in the future.

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