

Photoionization Detection (PID) as a High Throughput Screening Tool in Catalysis

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Abstract

A versatile photoionization detection (PID) system has been developed to rapidly screen libraries of catalytic materials. The PID approach involves the use of an appropriately selected DC discharge lamp to obtain monoenergetic photons, which are then used to photoionize gaseous molecules whose ionization potentials are lower than the photon energy. The suitability of the PID as a rapid screening tool has been demonstrated using oxidative dehydrogenation of ethane and propane as example reactions. Two 66 member ternary libraries of V-Mo-Li and V-Mo-Rb on γ -Al₂O₃ were tested for ethylene and propylene formation using the 10.6 eV photons from a Kr discharge lamp. The PID screening allowed the determination of 6% V, 3% Mo and 1% Li as the optimal catalyst formulation with regard to maximum alkene production for both reactions in a matter of hours.

Introduction

Combinatorial or high-throughput experimentation, where large diversities of materials are prepared, processed and screened for desired activity and selectivity in a rapid fashion is increasingly being used in heterogeneous catalysis research and development.^[1] However, in spite of impressive progress being made, it also became apparent that specific tools must sometimes be developed for specific applications.

A vital component of combinatorial catalysis is the availability of sensitive and robust high-throughput screening techniques. To date, a large number of screening methods have been developed and tested in combinatorial heterogeneous catalysis.^[1] Among the many methods developed, optical techniques and mass spectrometry have been most commonly used due to their broad applicability and speed.

Optical screening methods include infrared thermography,^[2] color indicators,^[3] laser fluorescence,^[4] resonance enhanced multiphoton ionization,^[5] photothermal deflection,^[6] laser induced fluorescence imaging,^[7] Fourier transform IR spectrometry.^[8] With the exception of the photothermal deflection (PTD) method, the most significant advantage of the optical methods is that they are noninvasive in-situ techniques, and as such do not require sample withdrawal. On the other hand optical methods provide limited specific product information or can be complicated and costly to implement.

Electron impact mass spectrometry (EIMS), on the other hand, is the most widely used screening technology in combinatorial catalysis because of its versatility, maturity and low cost.^[1] Nevertheless, the application of EIMS to certain types of reactions is limited when the fragmentation product(s) of abundant reactants overlap with those of reaction products. Industrially significant examples of such reactions, where EIMS is not useful,

include the oxidative dehydrogenation (ODH) of alkanes to form alkenes, such as ethane and propane dehydrogenations to ethylene and propylene, respectively. In both cases, the mass spectral patterns of the products totally overlap with those of the reactants, thereby ruling out the possibility to detect the desired ODH products by mass spectrometry. In fact, to address this problem the PTD was developed to screen catalysts for the ODH of ethane.^[6] The PTD approach involves the withdrawal of product gases from the ODH reactor and selectively heating the C₂H₄ molecules by a tunable IR laser. The resulting temperature gradient caused by the local and selective C₂H₄ heating is then measured by the deflection of a He-Ne probe laser. Although elegant, the practical implementation of the PTD approach is cumbersome and expensive. Consequently, the development of alternate methods that are easy to use and *inexpensive* to set up should greatly enhance our ability to screen ODH catalysts.

In this communication, we report on the development and use of a novel single photon ionization detection (PID) technique to screen libraries of catalytic materials. In PID, monoenergetic photons ($h\nu$) are used to ionize molecules whose ionization potentials (IP) are equal to or less than the impinging photons. This is indicated by the following photoionization reaction:



The photoions (P⁺) and the electrons (e⁻) generated are then collected by electrodes or collection plates positioned in close proximity of the light beam. Consequently, PID represents a generally applicable screening method for any reaction system in which the IP of the desired product is less than those of the reactants and other products. Clearly, if there are multiple species in the mixture whose IP are less than the energy of the incoming photons, the PID signal will correspond to the sum of all ions created by the photoionization process. Inexpensive discharge lamps can be used to generate monoenergetic photons. Lasers, which are more expensive, can also be used as photon sources. Readily available photon sources and energies include the chlorine lamp (8.9 eV), hydrogen lamp (10.2 eV), krypton lamp (10.6 eV) and argon lamp (11.8 eV).^[9] Photoionization detection is an extremely sensitive method that allows the detection of species well into the parts per billion (ppb) level.^[10-11] This high sensitivity is achievable because ions are easily collected and converted into laboratory signals, with very high signal-to-noise (S/N) ratios.

ODH of alkanes is particularly well suited for PID screening because the IP of alkenes are lower than the parent alkane.^[12] For example, the IP of ethylene and ethane are 10.5 eV and 11.5 eV, and those for propylene and propane are 9.73 eV and 10.96 eV, respectively.^[12] Thus, the use of an inexpensive krypton lamp, at 10.6 eV, can be used to selectively ionize ethylene in a mixture with ethane, and propylene in a mixture with propane.

The catalytic ODH of alkanes is one of the most vigorously pursued research topics of heterogeneous catalysis today using both traditional^[13-17] and combinatorial methodologies.^[6, 18-22] The screening methods used in the combinatorial ODH include gas

chromatography,^[18-20] combined EIMS and PTD^[6,21] and semiconductor gas sensors.^[22] Earlier studies also revealed that supported vanadium based materials to be promising catalysts for the ODH of C₂-C₄ alkanes.^[13,14,16,17] Combinations of unsupported V-Mo oxides were also found to be active especially for the ODH of ethane.^[13-17] In addition, alkali metals were reported to have a promotional effect on V/Al₂O₃ for the ODH of propane,^[16,23] but not for ethane.^[16] Furthermore, certain V based multi-component oxides on Al₂O₃ were noted to be active and selective ODH catalysts.^[13-24]

Considering these previous studies and to demonstrate the applicability of PID as a primary screening technique, we explored ternary combinations of V-Mo-Li and V-Mo-Rb supported on γ -Al₂O₃ as catalytic materials for the ODH of C₂H₆ and C₃H₈.

Experimental

Two 66 member ternary libraries of V-Mo-Li and V-Mo-Rb on γ -Al₂O₃ were prepared by the impregnation method. The total metal loadings were kept constant at 10 wt % with respect to the support material, while the loading of each component was varied between 0-10% in 1% intervals. First, aqueous stock solutions of active components were prepared by dissolving appropriate quantities of their salts in deionized water: LiNO₃ (Alfa Aesar), RbNO₃ (Alfa Aesar), (NH₄)₆Mo₇O₂₄ (Alfa Aesar), (NH₄)VO₃ (Alfa Aesar). Stock solutions were then dispensed into an array of vials using an automated liquid dispensation system described previously.^[25] After the preparation of the solution libraries, standard γ -Al₂O₃ tablets were introduced into the vials to affect impregnation for 72 h. The tablets were then dried at 80°C for 2h, 120°C for 2h and finally calcined at 500°C for 2 h by using a 1°C/ min heating rate prior to screening. Standard γ -Al₂O₃ tablets were prepared from commercial powder (Alfa Aesar) using a commercial tablet press (Stokes F1). Tablets were cylindrical in shape with dimensions of 0.4 cm diameter and 0.1 cm high. Each tablet weighed about 23 mg and possessed 150 m²/g BET surface area. All tablets were also pre-calcined at 500 °C for 2 h before impregnation.

Catalytic screening tests were performed using an array channel micro-reactor system described previously,^[25] and shown in Figure 1. Each reactor array consisted of 20 parallel rectangular channels that were micromachined on a flat non-porous silica ceramic slab. Each channel also possessed a cylindrical well to hold the catalyst pellets. Reaction gases passed through a series of baffles in the upstream and over the catalytic pellets in order to establish and maintain identical flow rates in each channel. In the current arrangement 4 microreactor arrays, each having 20 channels, were stacked and placed inside a stainless steel heating block. Thus it was possible to test the 66 combination ternary library, together with some duplicates and blank sites in a single experiment.

The concentrations of the reactants, products and the inert carrier gas were determined by withdrawing small streams from each microreactor channel using 2 parallel capillary sampling probes as shown in Figure 1. A 50 μ m ID capillary probe (C) was used to transfer gas samples directly to the mass spectrometer as reported previously.^[25] The second capillary (D) was 100 μ m ID, and was used to directly transfer gases to the PID

system. Upon entering the MS, gas samples were immediately subjected to 70 eV energy electrons and analyzed by the quadrupole (SRS, Sunnyvale, CA). The gas samples entering the PID were subjected to 10.6 eV photons from a Kr discharge lamp as shown in the insert of Figure 1 (0.2 W, RAE Systems, Sunnyvale, CA). The ions and electrons created were then collected by a pair of collection plates and the resulting ion currents were recorded with the aid of a voltmeter. The ionization volume of the PID that was swept by the sample gases was kept at about 0.10 cc, and gas flows in and out of the PID were adjusted to attain response times of about 2-8 s on a regular basis as shown in Figure 2. Thus PID has the capability to screen the entire 80 channel reactor block under 15 minutes, with the major time delay associated with the purging of the ionization volume. Clearly, this response time can be substantially reduced by the use of smaller ionization volumes and/or by increasing the gas flow rate through the ionization volume. Nevertheless, this high-speed feature of PID was not exploited in the present study since mass spectrometry, which is significantly slower, was also used to acquire data in parallel. Both the PID and EIMS were operated under the same operating and data acquisition software. PID signals were calibrated using known concentrations of C₂H₄ and C₃H₆ in mixtures under typical operating conditions prior to the testing of the catalytic materials. Each microreactor effluent was sequentially analyzed by moving the heated reactor block relative to the stationary sampling probes with the aid of a precision x-y-z positioning system.

It should be noted that the PID system described above can be modified to function as a parallel screening tool as well. This can be accomplished by simultaneously subjecting the reactor effluents to the ionizing photons and by measuring the resulting photoelectrons using microelectrodes placed within each channel in a manner similar to the REMPI approach reported previously.^[5]

Total feed gas flow rate varied between 50 to 300 sccm per array, which corresponds to GHSV range of ca. 10,000-60,000 h⁻¹ based on the volume of the standard catalyst pellets. The reactant mixture was composed of C₂H₆ or C₃H₈, and O₂, with different He dilutions. The specific feed gas compositions investigated were: C₂H₆ or C₃H₈: O₂: He = 2:1:2 and 2:1:7. Catalytic tests were performed at atmospheric pressure using a fresh set pellets and by systematically increasing the temperature from 300 to 500 °C in 50 °C increments. In order to ensure the establishment of steady state operating conditions after each change in set point temperature, a 20 min wait period was imposed before data acquisition. At a given set of operating conditions, the screening of the entire library by both PID and EIMS took about 1 h.

For the case of ethane ODH, C₂H₄ production was monitored quantitatively by the PID. In addition, EIMS was used to monitor the conversions of C₂H₆ (m/e=30) and O₂ (m/e=32), as well as the production of CO₂ (m/e=44). As will be discussed below, mass numbers 32 and 44, together with the PID signal represented a superior primary screening protocol for the ODH of ethane. However, the screening process for the ODH of propane was complicated by the possibility of formation of C₂H₄ as a by-product^[18-20] and the overlap of the mass spectral fingerprints of some of the participating species. Thus for the propane experiments, PID provides information on the sum of the products C₃H₆ and

C₂H₄. Nevertheless, the ability to monitor the combined signals of C₃H₆ and C₂H₄ still represent a useful primary activity-screening signal. In both C₂H₆ and C₃H₈ ODH, it was not feasible to monitor CO (m/e=28) using MS because of significant interference of this peak by the participating hydrocarbons and N₂ back diffusion from air.

Results and Discussion

The V-Mo-Li/ γ -Al₂O₃ library was first tested for ethane ODH. In Figure 3, an example of the raw data acquired by the PID and the MS is shown as a function of reactor site. As evident from Figure 2, both the PID and EIMS signals exhibited good signal-to-noise (S/N) ratios, providing unambiguous discrimination between different catalytic sites. However, the superiority of the PID signals is particularly noteworthy, by the high S/N ratios. Indeed, the high S/N ratio is one of the most prominent advantages of the PID and related techniques that exploit the creation and detection of ions.^[1,11]

It should be noted that only the mass signals 32 (O₂) and 44 (CO₂) are presented in Figure 3 due to their superior S/N ratios compared to mass 30 (C₂H₆). This is an expected result because O₂ was the limiting reactant. In other words, the fractional conversion of O₂ would be numerically higher than that of ethane, thus the mass 32 signal exhibit a higher S/N ratio than mass 30. Similarly, the mass 44 signal would be expected to exhibit good S/N ratio, as it is produced over a low background noise.

A close inspection of Figure 3 reveals that high levels of PID signals, indicative of C₂H₄ production, coincide with measurable conversions of O₂, as indicated by dips in O₂ intensity, and low levels of CO₂ production. On the other hand, O₂ conversions together with higher CO₂ levels, the latter being indicative of complete combustion, produced only low levels of C₂H₄ thus low PID signals, as seen for example at sites 3 and 62.

In Figure 4a the reactor exit gas concentrations of C₂H₄, expressed in parts per million (ppm) units, as determined by the PID are presented as a function of catalyst composition for the V-Mo-Li/Al₂O₃ library. The operating conditions leading to the results presented in Figure 4 were: temperature 425 °C, GSHV 30,000 h⁻¹, and feed gas composition He:C₂H₆:O₂ = 7:2:1. In Figure 4b, the relative concentrations of CO₂ produced by the same library are shown. As evident from Figure 4a, multielement combinations clearly exhibit superior ODH catalysis when compared to single element formulations. Most importantly, neither of the 3 metals used alone had any appreciable C₂H₄ forming activity, yet their combinations generated significant levels of ethylene under the experimental conditions investigated. It is particularly interesting to note that all binary catalysts involving vanadia exhibited maxima as a function of metal loading. On the other hand, binary combinations of Mo and Li were ODH inactive over the entire loading range investigated. The composition of the ternary catalyst that exhibited the maximum C₂H₄ productivity was V 6%, Mo 3% and Li 1%.

It should be noted that γ -Al₂O₃ supported V₂O₅ has a well documented ethane ODH activity.^[13-17] However, under the experimental conditions noted above, this catalyst did not show an appreciable C₂H₄ production (Figure 4a), while its CO₂ productivity was

high compared to other catalyst formulations (Figure 4b). On the other hand, at temperatures 450°C and higher, significant C₂H₄ production was also exhibited by vanadia catalysts. In fact at 500°C, the C₂H₄ productivity of the vanadia catalyst becomes comparable to other active catalysts in the library.

In Figure 5 the levels of C₂H₄ produced in the ODH of ethane for the V-Mo-Rb library are presented under the same operating conditions. As seen in this figure, the activity of Rb for the ODH of ethane was lower than that for Li, and this adversely affected the performance of all Rb-rich ternary catalytic materials. In fact, the optimal catalyst composition in this case was a binary combination of 5% V and 5% Mo.

The results in Figure 5 also demonstrate the reproducibility of the entire catalyst preparation and PID screening technique. For example, the V-Mo axis of the two libraries correspond to the same catalysts prepared separately. Therefore the results obtained for these catalytic materials should give an idea about the reproducibility of the entire methodology used. A comparison of the results presented in Figures 4 and 5 indicate that differences in PID measurements for these binary catalytic materials were less than 5%. This is an excellent result considering the large number of steps undertaken to prepare, process and tests these materials.

Experiments were also conducted under different conditions to explore the effects of temperature, flow rate and reactant gas dilutions. The results and trends obtained were similar to those presented in Figures 4 and 5. For example, the optimal ODH catalyst formulations remained 6% V, 3% Mo, 1% Li, and 5% V, 5% Mo.

The V-Mo-Li/ γ -Al₂O₃ library was also tested for the ODH of propane using the same experimental facility. In Figure 6, the measured PID signals, expressed as C₃H₆ are presented at the same operating conditions as the ethane experiments. As noted earlier, C₂H₄ can also form as a by-product in the ODH of propane.^[18-20] Since the 10.6 eV Kr lamp used ionizes both ethylene and propylene, the results are presented as C₃H₆ equivalent ppm. However, the use of a hydrogen discharge lamp (10.2 eV) can ameliorate this problem, and propylene (IP=9.73 eV) could be quantified without contributions from ethylene (IP=10.5 eV). As can be seen in Figure 6, multi-component catalysts again provided superior ODH catalysis compared to single component materials. However, in this case, the individual ODH activities of V/, Mo/ and Li/ γ -Al₂O₃ as well as their binary combinations were appreciable within the range of conditions investigated. The catalyst that produced the largest PID signal in the ODH of propane was V 6%, Mo 3% and Li 1%, the same material that was observed for the ODH of ethane.

In conclusion, the PID has been shown to be a fast and highly reproducible primary screening technique for the oxidative dehydrogenation of ethane and propane. The PID screening allowed the determination of a superior catalyst composition in the ternary libraries of V-Mo-Li/ γ -Al₂O₃ and V-Mo-Rb/ γ -Al₂O₃ in a short period of time, measured in hours, thereby demonstrating its utility as useful tool for the discovery and optimization of new catalytic materials.

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Table 1:List of catalytic materials and loading levels.

Cat#	V %	Mo %	Li or Rb %	Cat#	V %	Mo %	Li or Rb%
1	10	0	0	34	3	2	5
2	9	1	0	35	3	1	6
3	9	0	1	36	3	0	7
4	8	2	0	37	2	8	0
5	8	1	1	38	2	7	1
6	8	0	2	39	2	6	2
7	7	3	0	40	2	5	3
8	7	2	1	41	2	4	4
9	7	1	2	42	2	3	5
10	7	0	3	43	2	2	6
11	6	4	0	44	2	1	7
12	6	3	1	45	2	0	8
13	6	2	2	46	1	9	0
14	6	1	3	47	1	8	1
15	6	0	4	48	1	7	2
16	5	5	0	49	1	6	3
17	5	4	1	50	1	5	4
18	5	3	2	51	1	4	5
19	5	2	3	52	1	3	6
20	5	1	4	53	1	2	7
21	5	0	5	54	1	1	8
22	4	6	0	55	1	0	9
23	4	5	1	56	0	10	0
24	4	4	2	57	0	9	1
25	4	3	3	58	0	8	2
26	4	2	4	59	0	7	3
27	4	1	5	60	0	6	4
28	4	0	6	61	0	5	5
29	3	7	0	62	0	4	6
30	3	6	1	63	0	3	7
31	3	5	2	64	0	2	8
32	3	4	3	65	0	1	9
33	3	3	4	66	0	0	10

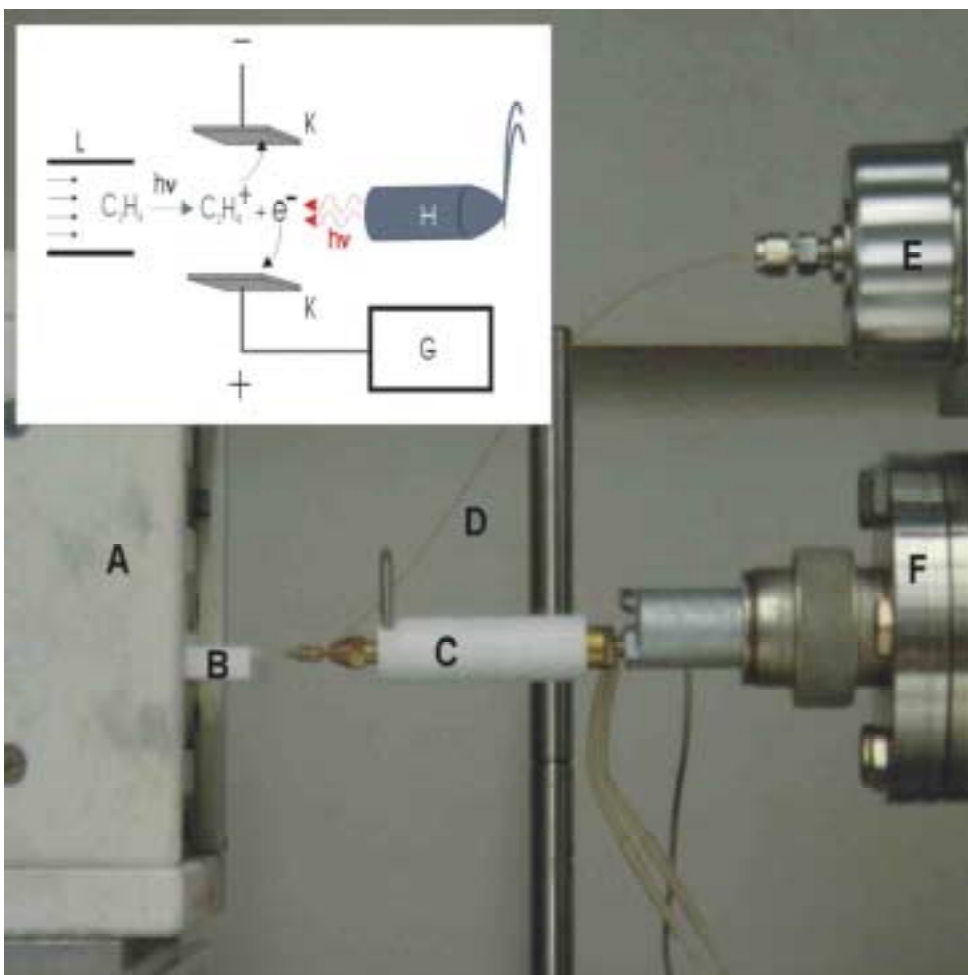


Figure 1. Picture of the experimental set up and the schematic of the PID principle. A: Heating block, B: Array channel microreactors, C: MS sampling probe, D: PID sampling probe, E: PID system, F: Mass spectrometer. *Insert of PID system:* G: Voltmeter, H: Kr Discharge Lamp, K: Ion collection plates, L: Sample feed line.

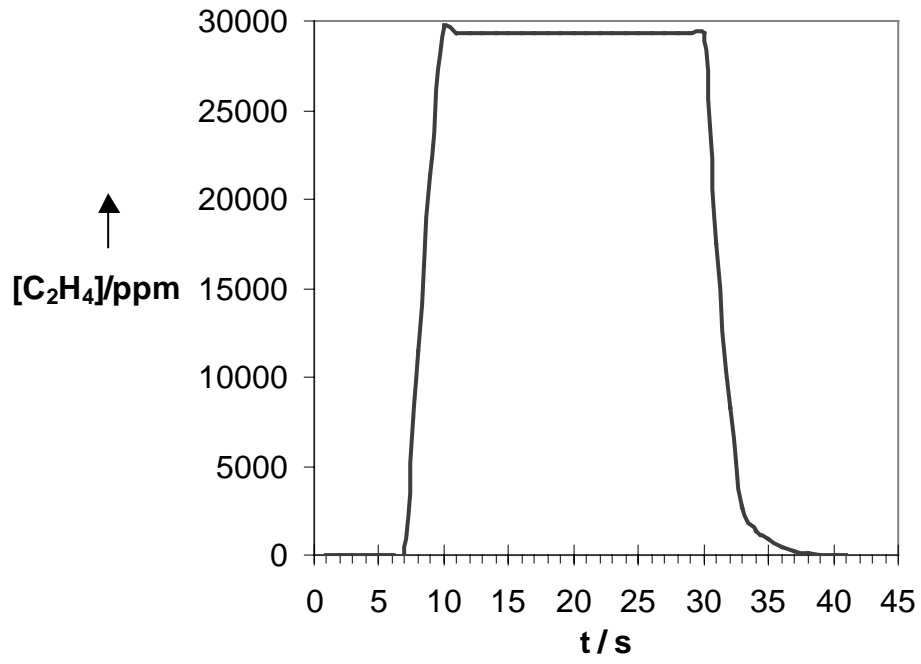


Figure 2. Temporal signal behavior of the PID system: $t=7\text{sec } C_2H_4$ on, $t=30\text{ sec } C_2H_4$ off

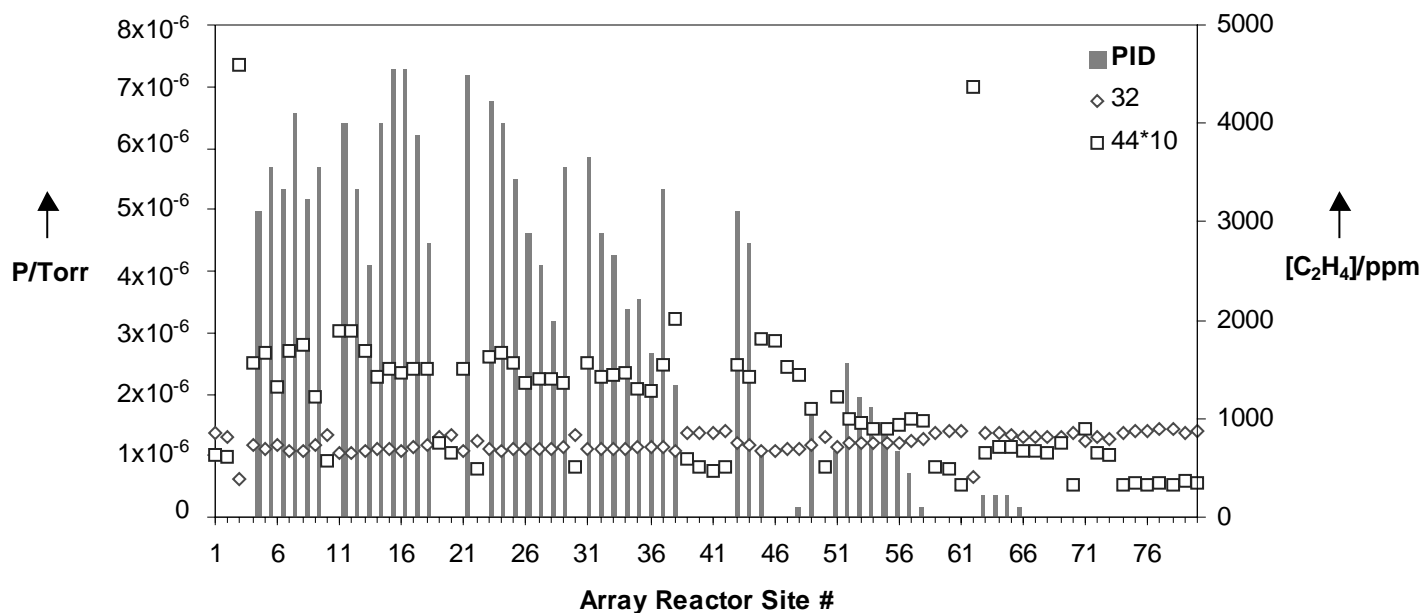


Figure 3. Raw experimental data for the EIMS and PID of VMoLi/Al₂O₃ Library; CO₂, (44 AMU), O₂(32 AMU) and PID Signal for C₂H₄. Experimental Conditions: T=425 °C, Feed; He:C₂H₆:O₂ (molar)=7:2:1, GHSV=30,000hr⁻¹. Sites 16 and 21, and 3 and 62 are duplicates, sites 1,2,10,20,30,40,41,50,60,61,70,80 are blank.

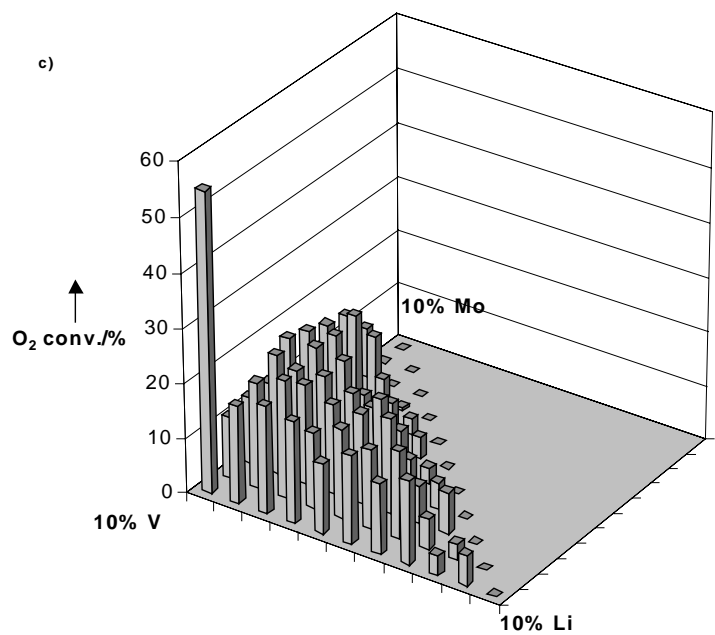
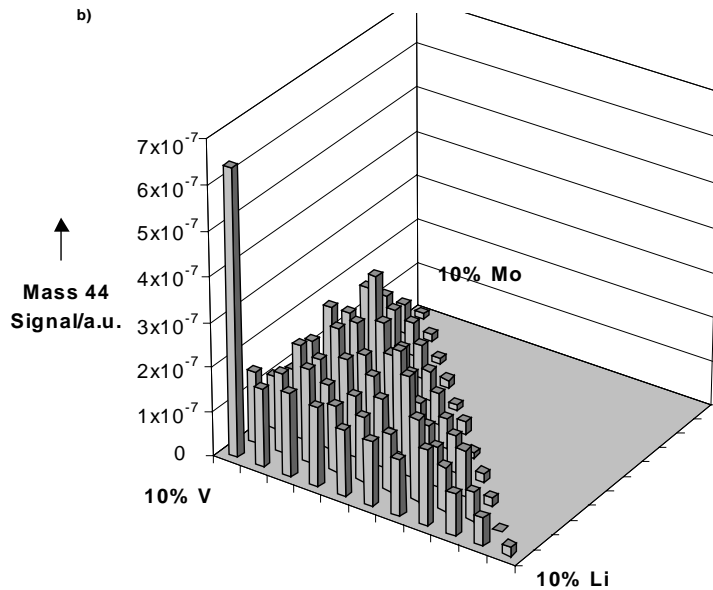
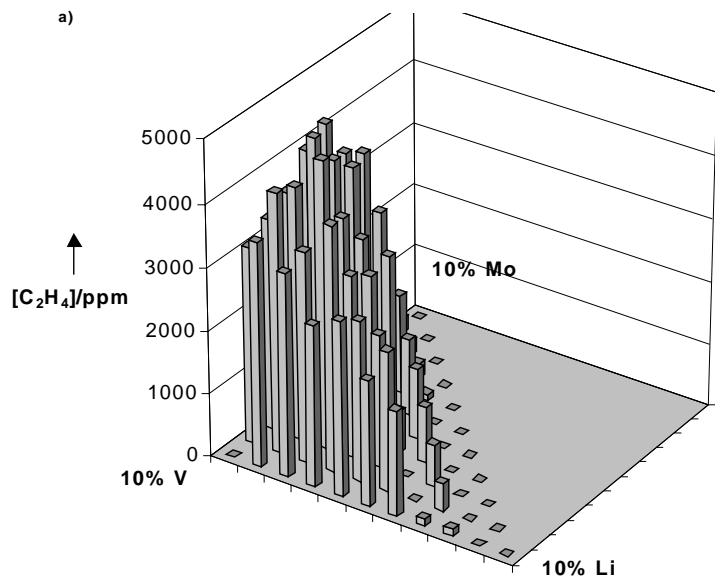


Figure 4. Results for the ODH of Ethane over V-Mo-Li/ Al_2O_3 Catalysts. $T=425\text{ }^\circ\text{C}$, $He/HC/O_2(\text{molar})=7/2/1$, $GHSV=30,000$.

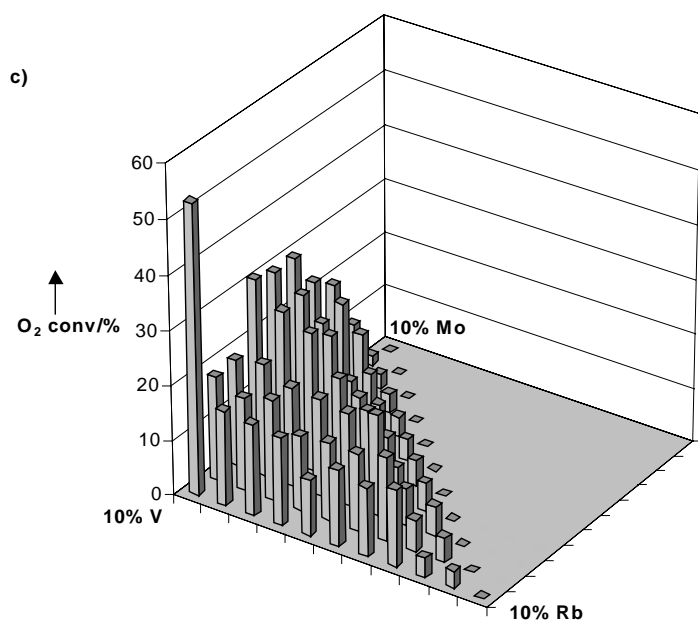
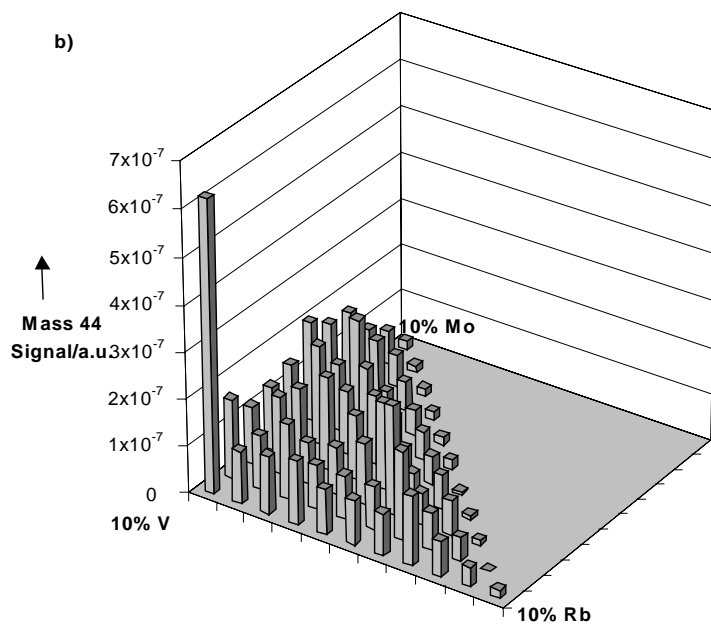
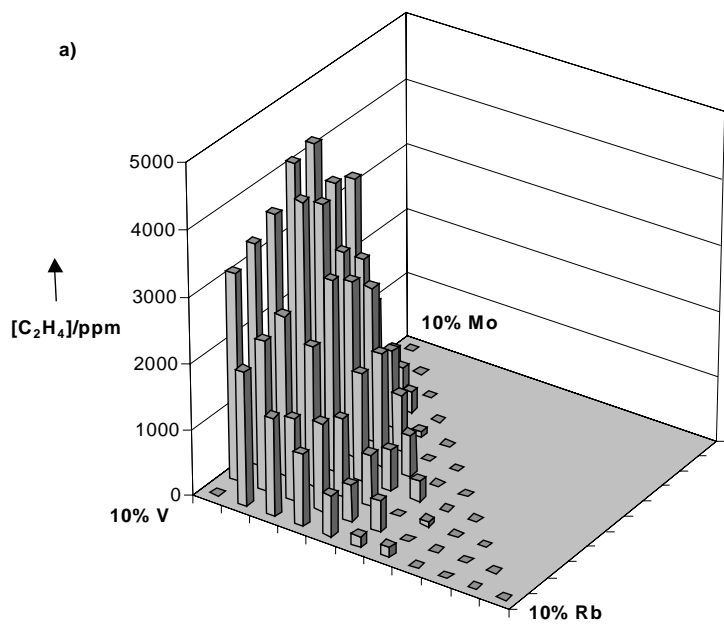


Figure 5. Results for the ODH of Ethane over V-Mo-Rb/ Al_2O_3 catalysts. $T=425$ °C, $He/HC/O_2$ (molar)=7/2/1, GHSV=30,000.

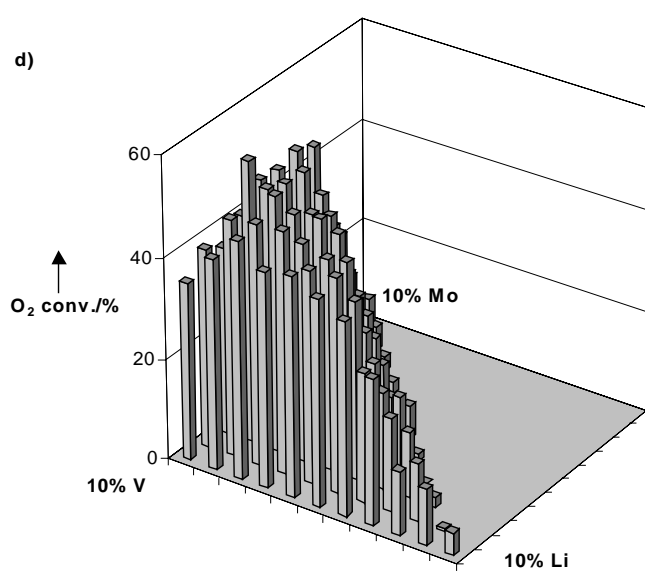
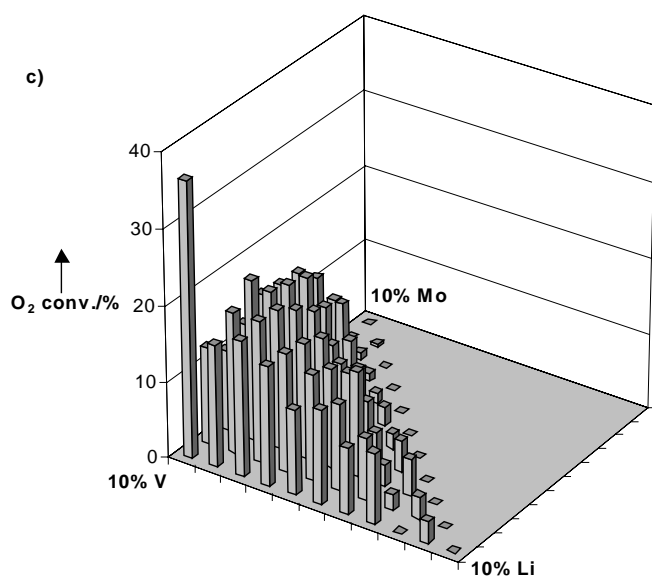
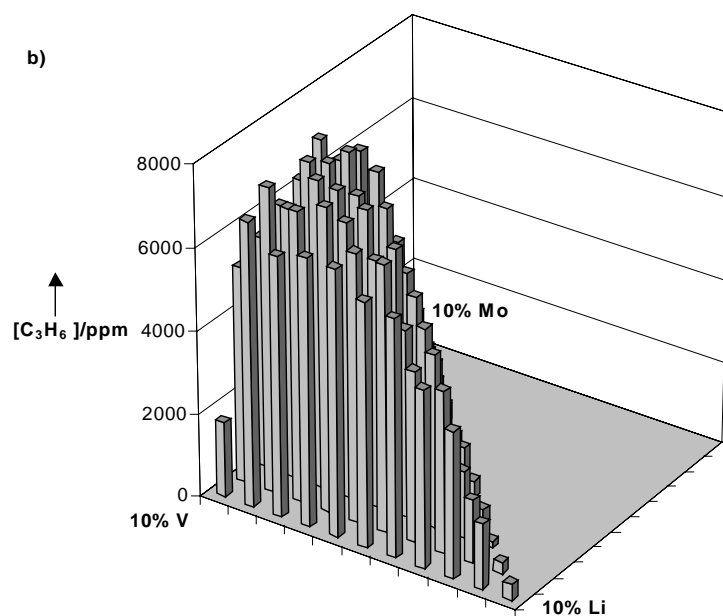
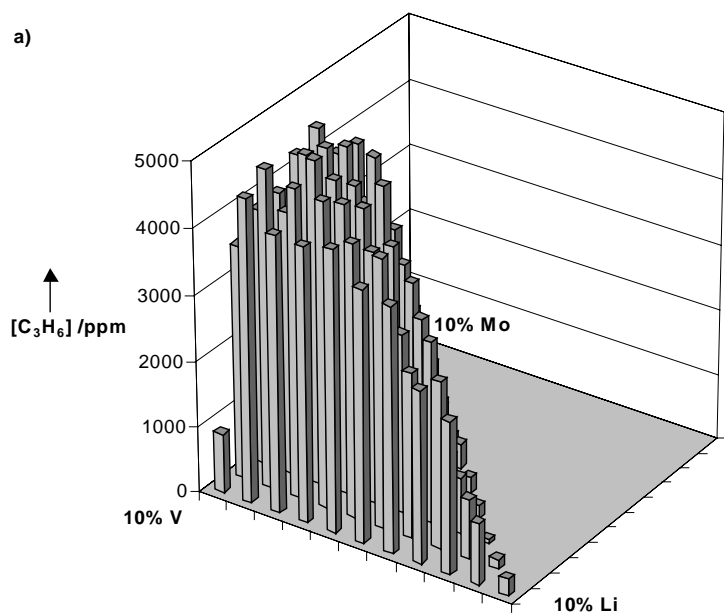


Figure 6. Results for the ODH of propane over V-Mo-Li/ Al_2O_3 catalysts. $T=400\text{ }^\circ\text{C}$, $He/HC/O_2(\text{molar})=7/2/1$ for a and c, $He/HC/O_2(\text{molar})=4/2/2$ for b and d GHSV=30,000.