

# Discovery of New Heterogeneous Catalysts for the Selective Oxidation of Propane to Acrolein

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**Abstract:** Combinatorial synthesis and screening technique have been applied to investigate the catalytic activity and selectivity of ternary and quaternary mixed-metal oxide catalysts for the selective oxidation of propane. The catalyst libraries were prepared *via* a modified sol-gel method using a synthesis robot and library design software, and examined for the catalytic activities in a simple high-throughput reactor system connected to a mass spectrometer for product analysis. Ternary Mo-Cr-Te, V-Cr-Sb, and Mo-V-Cr catalysts have been selected for potential candidate by composition spread approach. In a next generation composition spread library, the composition space of these three ternary compositions was sampled. Screening of this 198-member library provided substantial evidence that each ternary system has its own optimum composition where acrolein formation is highest. In addition, the composition space of the quaternary reference system Mo-V-Te-Nb mixed-oxides has also been prepared and sampled.

**Keywords:** Composition spread, high-throughput experimentation (HTE), propane, quaternary mixed-metal oxide, selective oxidation, sol-gel, ternary mixed-metal oxide.

## INTRODUCTION

Selective transformation of low molecular weight alkanes into more valuable products is a challenging task. The development of new catalysts for selective oxidation is considered promising. Acrylic acid (AA) and its esters are important monomers for the manufacture of homo- and copolymers, which are used mainly as surface protectants, in surface finishing, and as superabsorbents (super absorbent polymers, SAP) [1]. To date, the industrial production of acrylic acid involves a two-step process, which consists of the propene oxidation to acrolein (ACR) over multicomponent Mo-Bi-Co-Fe based oxide catalysts in the presence of steam and air at 330-370 °C and 1-2 bar followed by the oxidation of ACR to acrylic acid over Mo-V based oxide catalysts at 260-300 °C, with an overall yield of approximately 87 % [2]. A large amount of water is generally added to the reactant for the purpose of shift of explosion limit, improvement in desorption from catalyst, and facilitation of heat removal [1]. Propene is produced directly in the catalytic cracker from higher molecular weight fractions during petrochemical refinement of crude oil and by catalytic dehydrogenation from propane.

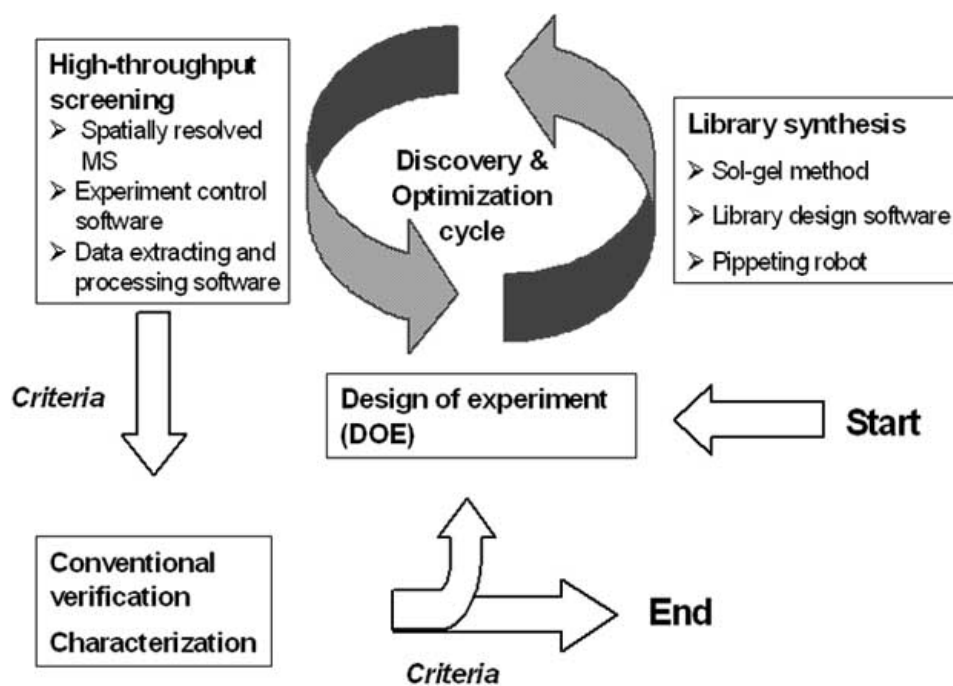
To substitute the production of propene and the current two-steps propene-to-acrolein and acrolein-to-acrylic acid process, the single-step direct oxidation of propane to AA has attracted growing attention in the past decade in both academia and industry. By now, three well-known categories of catalyst systems, vanadium pyrophosphate (VPO) type catalysts [3, 4], heteropoly compounds catalysts [5, 6] and multi-component or mixed metal oxides catalysts (MMO)

[7-9], have been extensively studied for the selective oxidation of propane to AA. Among these, MMO catalysts are commonly considered to have a possibility to replace the traditional catalysts in the existing industrial two-step process *via* propylene. Among those MMO catalysts systems, the most promising catalyst appears to be the Mo-V-Te-Nb mixed oxide, proposed by the Mitsubishi Chemicals, which is reported to achieve more than 40% of acrylic acid yield [10]. An appropriate Mo-V-Te-Nb metal ratio is critical for the formation of high catalytic activity.

Although Mo-V-Te-Nb and Mo-V-Sb-Nb mixed oxides are known to be effective for the selective oxidation of propane to AA, the catalytic performance is not yet sufficient for industrial applications. Therefore, substantial investigations of new catalytic system are necessary to find a more active or stable catalyst. Demand for the discovery of such a new viable catalyst leads to the combinatorial approach applying high-throughput technologies. The major advantage of the combinatorial approach lies in the possibility to test a large number of samples in a short time under comparable reaction conditions, which increases the chances of discovery of totally new and unexpected catalysts and their optimization. The development and application of high-throughput methods for the rapid discovery and optimization of solid-state catalysts has led to promising results during the last few years [11-23]. Since the technology available for the selective oxidation studies were not suitable to study the conversion to AA, the conversion of propane to ACR was selected as an indicator for the chances to find new catalysts for the reactions of interest.

In the present work, diverse libraries of MMO catalysts for the selective oxidation of propane to ACR were synthesized *via* a modified sol-gel method using a synthesis robot and library design software, and tested in a high-throughput

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**Fig. (1).** Flow chart of the high-throughput experimentation in the present study.

mass spectrometer (MS) screening setup described previously [16, 18-20].

## EXPERIMENTAL

### 1. High-Throughput Experiment

Efficient implementation of high-throughput experimentation (HTE) requires the complete combinatorial workflow with no bottleneck. The general strategy for high-throughput experimentation in the present study involves not only the discovery and optimization cycles with the creation and evaluation of catalyst libraries but also conventional verification and characterization. The typical HTE procedure in this study is demonstrated in Fig. 1. The discovery and optimization cycle containing library design, synthesis and performance testing is carried out until the most promising catalysts to satisfy the desired properties are found. The catalysts with promising results are reproduced and validated in a conventional manner, and the properties of the new catalysts are characterized. The knowledge extracted from the conventional confirmation and characterization is also used in the design of new libraries leading to another discovery and optimization cycle.

### 2. High-Throughput Syntheses of Catalyst Libraries

It is well known that the catalytic activity of heterogeneous catalysts is very sensitive to preparation conditions. The function of a catalyst is highly dependent on the exact synthesis protocol, the synthesis procedure, and the precursors used. Changing the sequence of additions and allowing different drying times and calcination temperatures will result in a variety of different materials of identical composition, but different catalytic activity and selectivity. Thus, variations in chemical composition with a wide range of elements must be carried out with a common synthesis procedure that is tolerant to such compositional changes. Many conventional catalyst preparations are not suitable for such a search.

Highly tolerant synthesis recipes have been developed, which allow the broad screening of elemental compositions based on sol-gel procedures [17, 18, 24]. These recipes have been used to prepare a large variety of mixed oxides, which can then be tested for catalytic performance. Because all catalyst materials were mixed oxides and the oxidation state of the oxides was not determined and may change during the experiment, the materials are identified only by the metal ions and atomic ratio given as a subscript; for example,  $\text{Mo}_{0.3}\text{Cr}_{0.7}$  means a mixed oxide comprising 30 molar % of Mo and 70% of Cr oxides.

Typically, 0.5 M metal precursor solutions except for molybdenum (0.1 M) and tungsten (0.226 M) were prepared by metal alkoxides (vanadium (V) triisopropoxide, iron (III) ethoxide, niobium (V) ethoxide, tantalum (V) ethoxide, manganese (II) propionate, tungsten (VI) isopropoxide in *i*-propanol, and bismuth (III) 2-ethylhexanoate, molybdenum (V) hexanoate in *n*-propanol), nitrates (chromium(III) nitrate in *i*-propanol) or anhydrous metal chlorides (antimony (V) chloride, tellurium (IV) chloride, niobium (V) chloride in *i*-propanol).

The automated synthesis of catalysts was done using a commercial pipetting robot (LISSY, Zinsser Analytic). In the procedure, the prepared metal solutions were positioned in 10 mL vials and used to formulate the final reaction mixture by transferring the aliquots of each stock solution into 2-mL vials, positioned in racks of 50 vials. The synthesis of the combinatorial catalyst libraries was accelerated using the Plattenbau library design software [25]. This software calculates, based on a parameterized recipe, the volumes of the different solutions of starting materials, as required for the preparation of the individual samples. It also generates an optimized pipetting list, which can be transferred directly to the pipetting robot.

For the synthesis of MMO catalysts, a modified acid catalyzed sol-gel method was applied, based on the proce-

ture described in detail previously [17, 18, 24]. The molar ratio of metal:water:acid (propionic acid):complexing agent (4-hydroxy-4-methyl-pentanone):alcohol (i-propanol) was 100:100:6:300:6500. The prepared samples are identified by the central elements with the expected mol% from the composition of the starting sol given in subscripts. The total molar amount of central elements was set as 200  $\mu\text{mol}$  per sample.

After the pipetting process of an entire rack (50 vials) was completed, this rack was covered and placed on an orbital shaker (Titramax 100; Heidolph) for 3 h. After removing the lid, the resulting sols were dried for 5 days at 40 °C to allow gel formation and catalyst drying. All samples were calcined in an oven at 65 °C for 5 h and at 250 °C for 5 h. The catalyst powders obtained were ground with a glass rod in the vials and manually transferred into 207 hexagonally positioned wells ( $\phi$  3.5 mm) in a stainless steel library plate ( $\phi$  99 mm). Some wells were left empty for background, and one well was filled with a reference catalyst ( $\text{Mo}_{0.6}\text{V}_{0.2}\text{Te}_{0.13}\text{Nb}_{0.07}$ , prepared by the conventional slurry method) for comparison. The activity of each well was represented relative to the activity of the reference catalyst. The prepared library was calcined again at 600 °C for 2 h in an oven with inert condition.

### 3. High-Throughput Testing of Catalyst Libraries

The open-well, high-throughput reactor system connected to a quadrupole mass spectrometer was used for a rapid sequential primary screening, which has been described in detail previously [16, 18, 20]. The catalyst library is placed in a special reactor with a heating system and insulation. In the reactor system, a capillary bundle containing both the educt gas supply and the product gas sampling system is inserted sequentially into each well of the library plate. The position of the capillary bundle is fixed while the complete reactor is moved by an xyz-stage. The high-throughput screening was controlled by the TestRig software by controlling xyz-stage movements and sampling [26].

The library plate temperature was set to 420 °C for each measurement. The composition of the reactant gas mixture was 8.7 vol%  $\text{C}_3\text{H}_8$ , 4.9 vol%  $\text{O}_2$ , 10 vol%  $\text{H}_2\text{O}$ , and Ar balance with a total flow rate of 5  $\text{ml min}^{-1}$ . A liquid mass flow controller (MFC) connected to an autoclave was used to inject desirable amounts of water. The injected water was well-mixed with reactant gas in a micro mixer (SSIMM, IMM). In addition, the whole educt and product line was heated with thin heating elements controlled by a thin thermocouple to prevent liquid condensation. The products were monitored on-line by a quadrupole mass spectrometer (GSD 300 T2, Balzers). The monitored products  $m/z$  were 18 (water), 29 ( $\text{C}_3\text{H}_8$ ), 40 (Ar), 41 ( $\text{C}_3\text{H}_6$ ), 44 ( $\text{CO}_2$ ), 55 (acrolein), and 72 (acrylic acid). The argon intensity was chosen for internal standardization as representative within the chronological progress recording the detection sensitivity over the whole experiment.

In a standard experiment, it took about 120 s (100 s inside the hole for reaction, 10 s outside the hole for waiting, and another 10 s for xyz-stage moving) to evaluate the catalytic activity for each material. Therefore, the activity test of 207 catalysts took approximately 7 h. The data obtained

were analyzed computationally with the software MS Express [27].

## RESULTS

### 1. Screening of A Library Containing Mixed Oxides Based on 11 Elements

In a first library, 11 elements were selected (Mo, V, Te, Ta, Nb, Sb, W, Cr, Bi, Mn, Fe). The selection was based on the interesting dehydrogenation and/or oxidation properties of the associated oxides. This library contained only ternary mixed oxides with a molar composition of (0.33, 0.33, 0.33), resulting different 165 catalysts as shown in Fig. 2. This library was calcined and activated as mentioned above, and library plate was loaded into a reactor and heated up to 420 °C. Since the primary screening was conducted at low propane conversion (less than 2%) due to short contact time, the concentration of reactant remain almost constant for all the catalysts screened. Therefore the activity and selectivity of catalysts screened only reflects their initial values, eliminating the complication caused by reactant depletion.

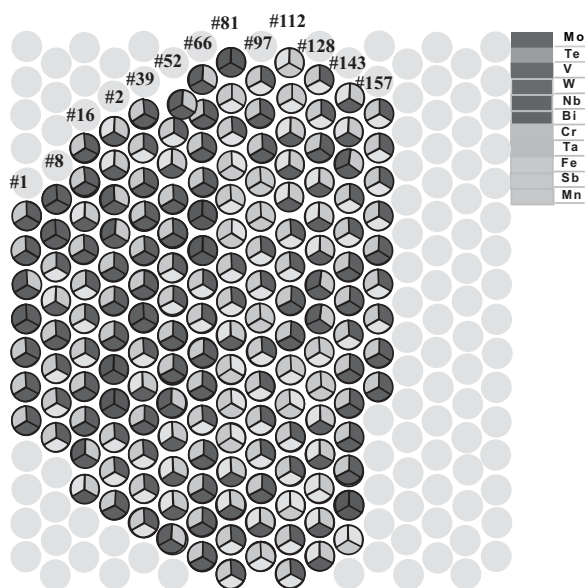
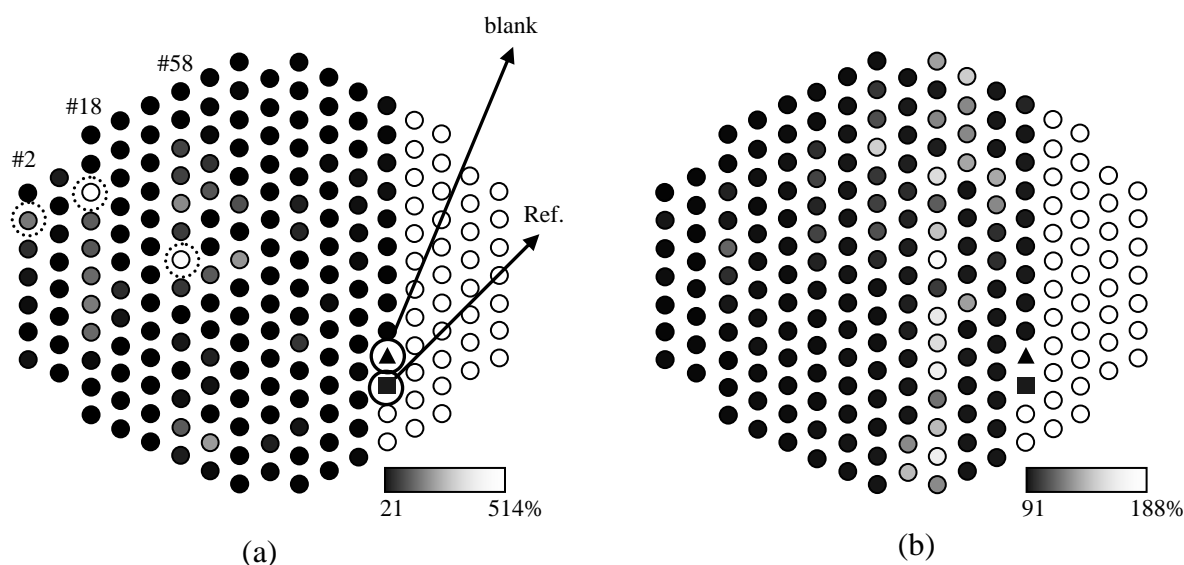


Fig. (2). Sample position of ternary mixed library and composition of each sample.

The high activities for the ACR formation are found at the Mo-Cr-Te (# 18, # is indicating channel number), V-Cr-Sb (#58), and Mo-V-Cr (#2) as shown in Fig. 3. In the figure presentation, the performance of reference catalyst ( $\text{Mo}_{0.6}\text{V}_{0.2}\text{Te}_{0.13}\text{Nb}_{0.07}$ ) was set to 100 % and a color tone was adjusted between the lowest and highest intensity of MS signal for ACR and  $\text{CO}_2$ . Maximum intensity of MS signal for ACR and  $\text{CO}_2$  was set to white and minimum intensity of MS signal for ACR and  $\text{CO}_2$  was set to black irrespective of percentage. The  $\text{Mo}_{0.33}\text{Cr}_{0.33}\text{Te}_{0.33}$  and  $\text{V}_{0.33}\text{Cr}_{0.33}\text{Sb}_{0.33}$  catalysts show high ACR formation and relatively low  $\text{CO}_2$  formation. About 25 % of the prepared samples from the library produced more  $\text{CO}_2$  than the reference catalysts. Because the  $\text{CO}_2$  is product originated from undesirable total oxidation reaction, these samples have been excluded from further studies. The formation of AA was negligible for all the sam-



**Fig. (3).** Relative performance of ternary mixed oxides catalyst library at 420 °C (a) ACR, (b) CO<sub>2</sub> formation. The composition of #2, 18, and 58 is Mo<sub>0.33</sub>V<sub>0.33</sub>Cr<sub>0.33</sub>, Mo<sub>0.33</sub>Cr<sub>0.33</sub>Te<sub>0.33</sub>, and V<sub>0.33</sub>Cr<sub>0.33</sub>Sb<sub>0.33</sub>, respectively.

ples except for catalyst of identical composition as the reference catalysts, but prepared by the sol-gel procedure. The best catalysts towards ACR with low CO<sub>2</sub> formation are listed in Table 1.

**Table 1. Results for Different Ternary Bulk Oxide Catalyst Tested in a High-Throughput MS Reactor**

Catalyst	Rel. C <sub>3</sub> H <sub>8</sub> Conversion to ACR (%)	Rel. C <sub>3</sub> H <sub>8</sub> Conversion to CO <sub>2</sub> (%)
(# 2) Mo <sub>0.33</sub> V <sub>0.33</sub> Cr <sub>0.33</sub>	286	95
(# 18) Mo <sub>0.33</sub> Cr <sub>0.33</sub> Te <sub>0.33</sub>	508	103
(# 58) V <sub>0.33</sub> Cr <sub>0.33</sub> Sb <sub>0.33</sub>	488	104
(# 89) Fe <sub>0.33</sub> Cr <sub>0.33</sub> W <sub>0.33</sub>	236	108
(# 56) V <sub>0.33</sub> Cr <sub>0.33</sub> Mn <sub>0.33</sub>	248	126
Reference	100	100

## 2. Screening of the Newly Prepared Library Composed of MoCrTe, VCrSb, and MoVCr

Based on the results of the library of ternary mixed oxides composed of 11 elements, we have chosen the MoCrTe, VCrSb, and MoVCr as potential catalysts for the propane oxidation to ACR or AA. A spread of the composition library was prepared, where all the three elements were allowed to vary between 0 and 100 mol% in steps of 10 mol%. Each library contains 66 discrete compositions and thus a total of 198 samples with the various compositions of ternary samples were obtained as shown in the Fig. 4. The sample powders were dried and calcined in the same way as mentioned above and then catalytic performance was screened.

### 2.1. Catalytic Activity Test of VCrSb Oxides

Fig. 5 illustrates the performance of the ternary mixed oxides of V-Cr-Sb. The three corners in this figure corre-

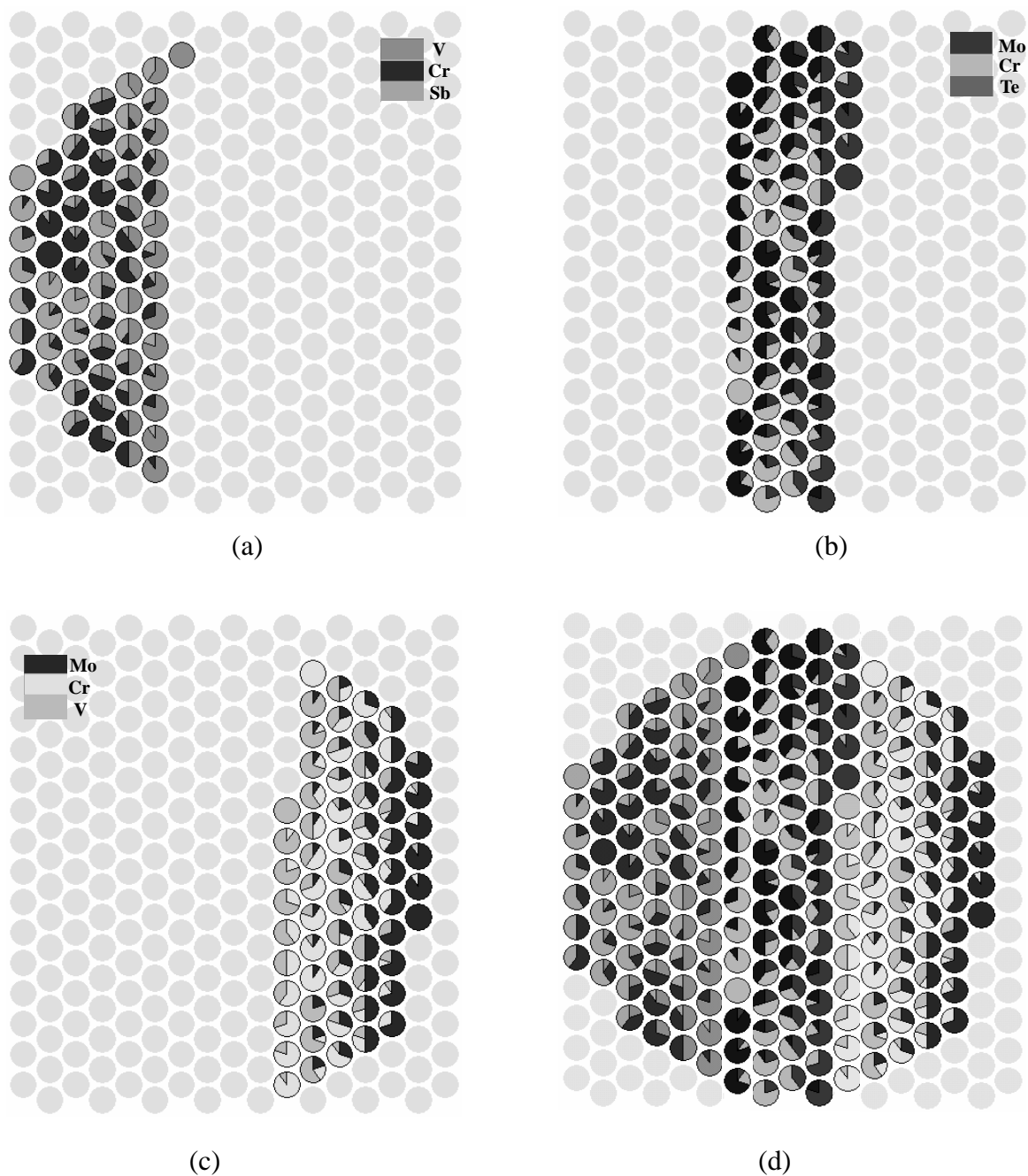
spond to 100% V, 100% Cr, and 100% Sb, respectively. The composition increment is therefore 10% per matrix element. The data clearly show a high activity for the ACR formation is near the composition of V<sub>0.1-0.4</sub>Cr<sub>0.3-0.4</sub>Sb<sub>0.2-0.6</sub> (Fig. 5a). The most active catalyst is V<sub>0.2</sub>Cr<sub>0.2</sub>Sb<sub>0.6</sub> which shows about 250 % higher ACR formation compared to the reference catalyst. The CO<sub>2</sub> formation as shown in the Fig. 5b is increased in the region V<sub>0-0.1</sub>Cr<sub>0.6-0.9</sub>Sb<sub>0.1-0.3</sub>, which indicates that the total oxidation is major reaction in this region and selectivity does not correlate with elemental composition.

### 2.2. Catalytic Activity Test of MoCrTe Oxides

Fig. 6 shows the performance of the ternary mixed oxides of Mo-Cr-Te. The highest activity for ACR formation is observed at Mo<sub>0.3-0.4</sub>Cr<sub>0.4-0.5</sub>Te<sub>0.1-0.2</sub> (Fig. 6a). The most active catalyst in this region is found at Mo<sub>0.3</sub>Cr<sub>0.5</sub>Te<sub>0.2</sub>. This catalyst is much more active, which shows 480 % higher activity for ACR formation compared to the reference catalyst. Fig. 6b shows that the total oxidation mainly occurs at the chromium rich regions, indicating some element-specific selectivity.

### 2.3. Catalytic Activity Test of MoVCr Oxides

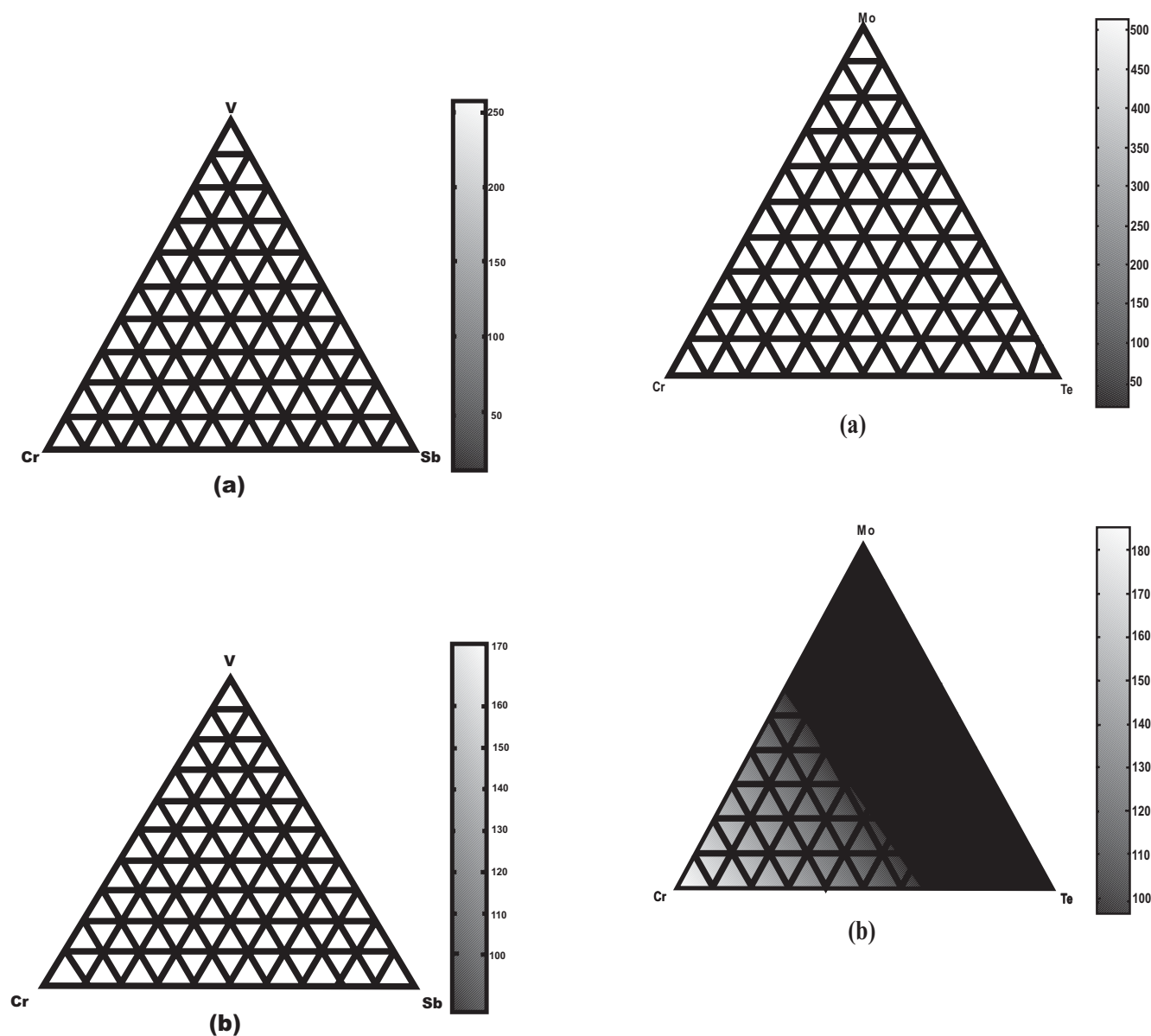
The relative performance of the ternary mixed oxides of Mo-V-Cr is depicted in the Fig. 7. In this case, the catalytic activity is sensitive to the catalyst composition, with those along the Mo and Cr binary axis and V and Cr axis with small amount of Mo producing high amount of ACR. The highest activity for the ACR formation is found in the region with Mo<sub>0.1-0.4</sub>V<sub>0-0.3</sub>Cr<sub>0.5-0.7</sub> (Fig. 7a). The most active catalyst for ACR formation is Mo<sub>0.3</sub>Cr<sub>0.7</sub> which shows 250 % higher activity than the reference catalyst. The CO<sub>2</sub> formation is observed only in the chromium rich region similar to the VCrSb and MoCrTe oxides. It was found that the VCrSb, MoCrTe, MoVCr oxides systems show promising catalytic performance for the direct formation of ACR associated with a reduced activity for CO<sub>2</sub> formation (chemoselectivity). The highest CO<sub>2</sub> formation was found at chromium rich region which can be conjectured as good total oxidation catalysts.



**Fig. (4).** Ternary library composition and position of (a) VCrSb oxides, (b) MoCrTe oxides, (c) MoVCr oxides, and (d) whole spread with 0 ~ 100% Mo, 0 ~ 100% V, 0 ~ 100% Cr, 0 ~ 100% Te, 0 ~ 100% Sb in 10% increments.

The major product ACR is an important industrial chemical used as an intermediate to produce AA or methionine an aminoacid used for the poultry feeding. In literature there are some reports on direct oxidation of propane to ACR [28-31]. For instance, the  $\text{Mo}_{1.3}\text{V}_{0.3}\text{Te}_{0.3}\text{O}_x/\text{MCM-41}$  catalyst appeared to be interesting with ca. 16% yield of

ACR [31]. The active metal components of Mo, V, Te are well known where the Mo oxide was regarded to favor the formation of partial oxidation product, V oxide to promote the activation of C-H bond, and the Te oxide, particularly  $\text{Te}^{4+}$  is responsible for the H-abstraction from propene and O-insertion into allyl species, which is a reaction intermedi-



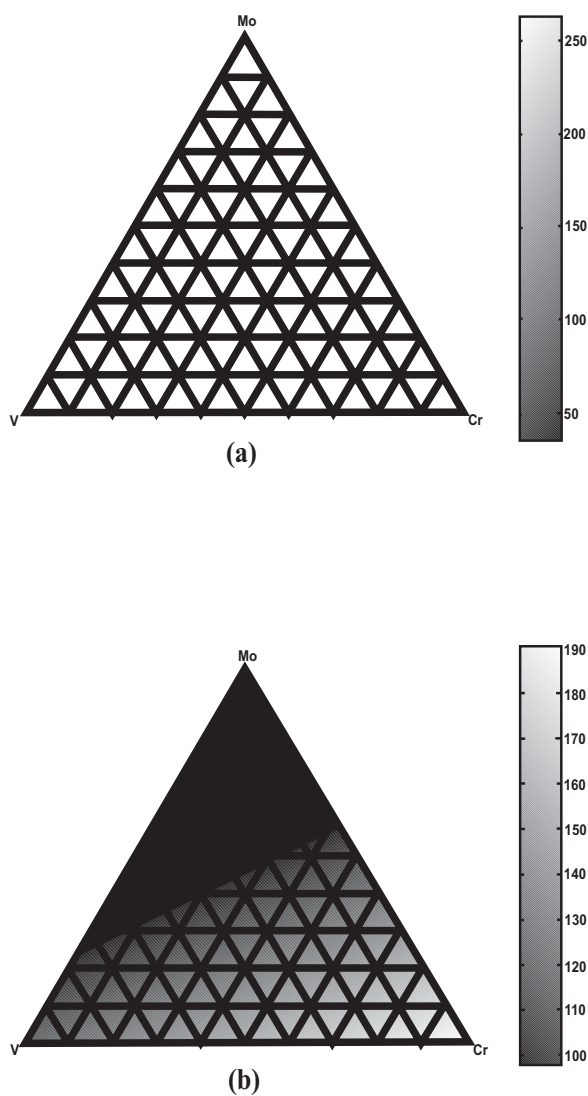
**Fig. (5).** Relative performance of 66 member V-Cr-Sb oxides (a) ACR, (b) CO<sub>2</sub>.

ate [30]. On the other hand, the effect of Cr oxide on the selective oxidation of propane selective oxidation to ACR has not been reported yet. Generally, Cr-containing catalysts are one of the most effective catalysts for the partial oxidation of methane to methanol/formaldehyde [32, 33], cycloalkanes to cycloalkenes [34], and *n*-butane to maleic anhydride [35]. Han *et al.*, reported that Cr oxide improves the conversion of methane in partial oxidation for methanol and formaldehyde and combining Mo (VI) and Cr (III) oxides appear to be favor the formation of partial oxidation product [36]. Even though the effect of Cr oxide on the propane partial oxidation is not clear, it is speculated that smaller amounts of Cr oxide combining with Mo-V, Mo-Te, and V-Sb enhance the selectivity to ACR formation by reducing CO<sub>2</sub> formation.

**Fig. (6).** Relative performance of 66 member Mo-Cr-Te oxides (a) ACR, (b) CO<sub>2</sub>.

### 3. Optimization of Quaternary Mixed Oxides

It is well known that quaternary mixed oxides composed of Mo-V-Te-Nb are the most promising composition for AA formation. Selective oxidation of propane over the Mo-V based mixed oxide catalysts modified with Te and Nb were also found active for the propane oxidation to ACR [20]. Based on these facts, we prepared the quaternary mixed oxide catalyst library where Mo was allowed to vary between 50 ~ 100 mol%, while Nb was changed between 0 ~ 20 mol%, V and Te was 0 ~ 30 mol%, in the steps of 5 mol%, resulting in total of 190 samples. Fig. 8 summarizes the performance of the composition spread of the quaternary mixed oxides of Mo-V-Te-Nb. The highest activity for the ACR formation is found at the region of Mo<sub>0.65-0.8</sub>V<sub>0.1-0.25</sub>Te<sub>0.05</sub>Nb<sub>0.05-0.1</sub> (Fig. 8a). The most active catalyst for ACR formation is Mo<sub>0.7</sub>V<sub>0.25</sub>Te<sub>0</sub>Nb<sub>0.05</sub>, which shows 145 % higher



**Fig. (7).** Relative performance of 66 member Mo-V-Cr oxides (a) ACR, (b) CO<sub>2</sub>.

ACR formation compared to the reference catalyst. In addition, the formation of CO<sub>2</sub> (Fig. 8b) was low at high active regions where the formation of ACR is high. The best catalysts towards ACR with low CO<sub>2</sub> formation are listed in Table 2.

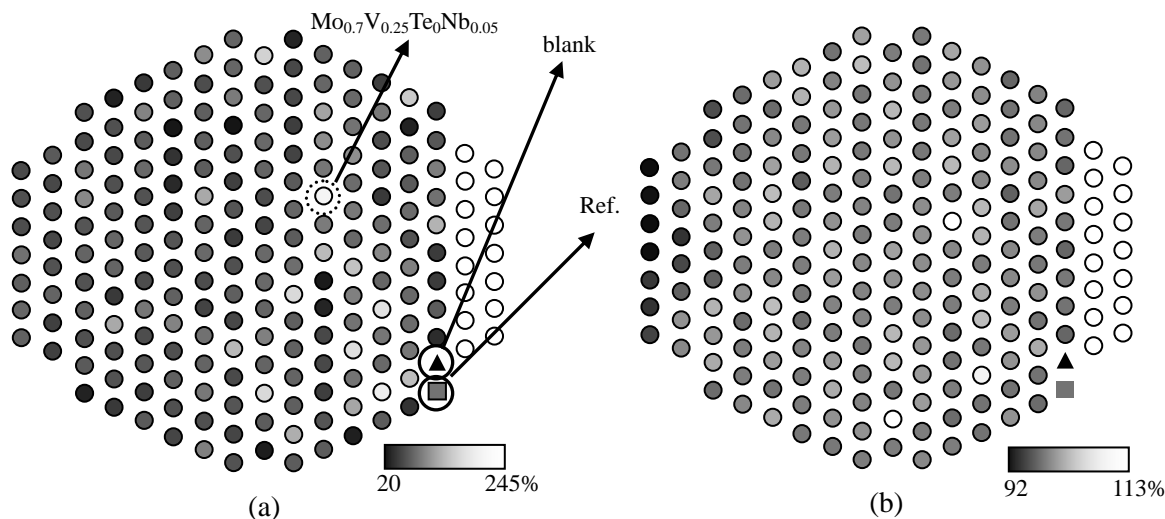
**Table 2.** Results for Bulk Oxide Catalyst of Quaternary Library Tested in a High-Throughput MS Reactor

Catalyst	Rel. C <sub>3</sub> H <sub>8</sub> Conversion to ACR (%)	Rel. C <sub>3</sub> H <sub>8</sub> Conversion to CO <sub>2</sub> (%)
(#133) Mo <sub>0.7</sub> V <sub>0.25</sub> Te <sub>0</sub> Nb <sub>0.05</sub>	245	102
(#109) Mo <sub>0.65</sub> V <sub>0.3</sub> Te <sub>0</sub> Nb <sub>0.05</sub>	208	105
(#153) Mo <sub>0.75</sub> V <sub>0.2</sub> Te <sub>0</sub> Nb <sub>0.05</sub>	215	100
(#165) Mo <sub>0.8</sub> V <sub>0.1</sub> Te <sub>0</sub> Nb <sub>0.1</sub>	220	108
(#168) Mo <sub>0.8</sub> V <sub>0.15</sub> Te <sub>0</sub> Nb <sub>0.05</sub>	235	126
Reference	100	100

However, formation of AA is still negligible except for the reference catalysts. It seems that different preparation methods make an effect on metal oxidation state and bulk phase of catalysts, resulting in different products. The lack of AA-formation may in part be attributed to the experimental set-up since AA has a low vapor pressure and does not diffuse effectively through the capillary connecting the HT-reactor with the mass spectrometer.

## CONCLUSION

We have screened about 600 samples consisting of ternary and quaternary mixed oxides for the propane selective oxidation by applying a combinatorial approach. We found that Cr containing ternary mixed oxides such as VCrSb, MoCrTe, MoVCr are potential candidates for the direct formation of ACR from propane. It was also found that, Mo<sub>0.3</sub>Cr<sub>0.7</sub> in the MoVCr mixed oxide system shows a high ACR formation even though it is a binary composition. In the quaternary compositions, Mo<sub>0.7</sub>V<sub>0.25</sub>Te<sub>0</sub>Nb<sub>0.05</sub> showed the highest ACR formation. However, AA formation is negligible.



**Fig. (8).** Relative performance of quaternary mixed oxides (MoVTeNb) catalyst library at 420 °C (a) ACR, (b) CO<sub>2</sub> formation.

Although we observed some remarkable findings from Cr-containing ternary mixed oxide catalysts for higher ACR formation and selectivity by using the high-throughput screening method, further detailed analysis and experimentation are required to elucidate more precisely the effect of Cr on the ACR formation in the selective oxidation of propane.

In primary screening, experimental conditions may differ significantly from conventional reaction conditions, accuracy and reproducibility of conversion or activity data are lower than conventional test. Due to this reason, scale-up of preparation of the optimal catalyst composition (hit samples) and testing in conventional gas-phase flow should be performed for validation of the results of the screening experiments. This validation test of primary screening and conventional testing could give a chance to find out the relationship between different metal compositions and catalytic performance.

#### ACKNOWLEDGEMENTS

This work is supported by the Center for Ultramicrochemical Process Systems sponsored by KOSEF (2004-2005). We thank Rudolf Richter and Heike Hölzten for help with the experimental set up and analysis, Simone Sieg for visualization and activity plot, and Michael Mentges for catalyst pretreatment.

#### REFERENCES

- [1] Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, Wiley-VCH: Weinheim, **2003**.
- [2] Voge, H.H.; Adams, C.R. *Adv. Catal.*, **1967**, *17*, 151.
- [3] Ai, M. *J. Catal.*, **1986**, *101*, 389.
- [4] Kerler, B.; Martin, A.; Paul, M.M.; Baerns, M. *Catal. Lett.*, **2002**, *78*, 259.
- [5] Mizuno, N.; Tateishi, M.; Iwamoto, M. *Appl. Catal. A*, **1995**, *128*, 165.
- [6] Ueda, W.; Suzuki, Y. *Chem. Lett.*, **1995**, *7*, 541.
- [7] Kaddouri, A.C.; Mazzochia, C.; Derouane, E.J. *J. Catal.*, **2002**, *211*, 226.
- [8] Manhua, L.; Michael-W, L.; A process for preparing a multi-metal oxide catalyst; **1999**. European Patent Office serial number 0,962,253, A2.
- [9] Baca, M.; Pigamo, A.; Dubios, J.L.; Millet, J.M.M. *Top. Catal.*, **1999**, *23*, 39.
- [10] Takashi, U.; Kazunori, O.; Production of alpha, beta-unsaturated carboxylic acid; **1998**. Japan Patent Office serial number 10-36311.
- [11] Maier, W.F. *Angew. Chem. Int. Ed.*, **1999**, *38*, 1216.
- [12] Senkan, S. *Angew. Chem. Int. Ed.*, **2001**, *40*, 312.
- [13] Woo, S.I.; Kim, K.W.; Cho, H.Y.; Oh, K.S.; Jeon, M.K.; Tarte, N.H.; Kim, T.S.; Mahmood, A. *QSAR Comb. Sci.*, **2005**, *24*, 138.
- [14] Hendershot, R.J.; Snively, C.M.; Lauterbach, J. *Chem. Eur. J.*, **2005**, *11*, 806.
- [15] Oh, K.S.; Park, Y.K.; Woo, S.I. *Rev. Sci. Instrum.*, **2005**, *76*, 062219.
- [16] Orschel, M.; Klein, J.; Schmidt, H.-W.; Maier, W.F. *Angew. Chem. Int. Ed.*, **1999**, *38*, 2791.
- [17] Paul, J.S.; Urschey, J.; Jacobs, P.A.; Maier, W.F.; Verpoort, F. *J. Catal.*, **2003**, *220*, 136.
- [18] Kim, D.K.; Maier, W.F. *J. Catal.*, **2006**, *238*, 142.
- [19] Hagemeyer, A.; Jandeleit, B.; Liu, Y.; Poojary, D.M.; Turner, H.W.; Volpe Jr., A.F.; Weinberg, W.H. *Appl. Catal. A*, **2001**, *221*, 23.
- [20] Weiss, P.-A.W.; Saalfrank, J.W.; Scheidtmann, J.; Schmidt, H.-W.; Maier, W.F. in *High Throughput Analysis: A Tool for Combinatorial Materials Science*; Potyrailo, R.A.; Amis, E.J. Eds.; Kluwer Academic/Plenum Publishers, New York, **2003**; Nov., pp. 125-153.
- [21] Wennemers, H. *Comb. Chem. High Throughput Screen.*, **2001**, *4*, 273.
- [22] Choi, W.C.; Jeon, M.K.; Kim, Y.J.; Woo, S.I.; Hong, W.H. *Catal. Today*, **2004**, *93-95*, 517.
- [23] Liu, J.H.; Jeon, M.K.; Woo, S.I. *Appl. Surf. Sci.*, **2006**, *252*, 2580.
- [24] Klein, J.; Maier, W.F. *Chem. Mater.*, **1999**, *11*, 2584.
- [25] Scheidtmann, J.; Saalfrank, W.J.; Maier, W.F. *Stud. Surf. Sci. Catal.*, **2003**, *145*, 13.
- [26] Scheidtmann, J.; Entwicklung und Anwendung kombinatorischer Methoden zur Entdeckung resistiver Gassensoren; Ph. D thesis, Universität des Saarlandes, **2003**.
- [27] Weiss, P.-A.W.; Thome, C.; Maier, W.F. *J. Comb. Chem.*, **2004**, *6*, 520.
- [28] Botella, P.; Nieto, J.M.L.; Solsona, B. *Catal. Lett.*, **2002**, *78*, 383.
- [29] Zhang, Q.; Wang, Y.; Ohishi, Y.; Shishido, T.; Takehira, K. *Chem. Lett.*, **2001**, *3*, 194.
- [30] Huang, C.; Jin, Y.; Ying, F.; Wan, H. *Chem. Lett.*, **2006**, *35*, 606.
- [31] Chen, L.; Liang, J.; Weng, W.; Wang, Y.; Wan, H.; Védrine, J.C. *Catal. Commun.*, **2004**, *5*, 697.
- [32] Zhang, Q.; He, D.; Han, Z.; Zhang, X.; Zhu, Q. *Fuel*, **2002**, *81*, 1599.
- [33] McCormick, R.L.; Alptekin, G.O.; Herring, A.M.; Ohno, T.R.; Dec, S.F. *J. Catal.*, **1997**, *172*, 160.
- [34] Samanta, S.; Mal, N.K.; Bhaumik, A. *J. Mol. Catal. A*, **2005**, *236*, 7.
- [35] Pierini, B.T.; Lombardo, E.A. *Catal. Today*, **2005**, *107-108*, 323.
- [36] Han, Z.S.; Pan, W.; Pan, W.X.; Li, J.L.; Zhu, Q.M.; Tin, K.C.; Wong, N.B. *Korean J. Chem. Eng.*, **1998**, *15*, 496.