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Combinatorial screening and conventional testing of antimony-rich selective oxidation catalysts

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Abstract

The use of high-throughput synthesis and screening techniques is demonstrated with the optimization of and the search for new antimony-rich mixed-metal oxide catalysts for the selective oxidation of isobutane to methacrolein. Three 207-member catalyst libraries have been prepared via a sol-gel synthesis procedure using design software and a synthesis robot. The catalyst libraries have been examined for catalytic activity and selectivity using spatially resolved mass spectrometry in an open-well reactor system. The reaction products have been detected by mass spectrometry and the massive data obtained have been analyzed with the help of dedicated software. Using a composition spread approach, an optimal composition of Mo–V–Sb catalysts has been identified. Screening of 68 combinations of other antimony-rich mixed oxides on libraries provides evidence that the Mo–V–Sb system is a unique ternary composition for selective oxidation of isobutane to methacrolein. Scale up of the combinatorially interesting compositions confirmed unequivocally their excellent catalytic behavior.

Keywords: Isobutane; Oxidation; Gas phase; Heterogeneous catalysis; Combinatorial chemistry; High-throughput experimentation (hte); Mo–V–Sb; Mixed oxides; Sol–gel process; Composition spread

1. Introduction

Selective oxidation is one of the most important strategies for the transformation of raw materials into more valuable components, since they produce worldwide about 25% of the industrial organic chemicals and intermediates used for the production of fine chemicals, pharmaceuticals, etc. [1]. Since the development of the process for the synthesis of maleic anhydride from n-butane in 1974 many research efforts have been devoted to the use of light paraffins. These processes not only offer economical advantages compared with the conventional processes but could also contribute to the growing interest in a green/sustainable chemistry.

A large variety of catalysts has been studied for the direct oxidation of isobutane to methacrolein and methacrylic acid. The most extensively studied systems are the heteropolyacid (HPA) catalysts [2–9]. One of the best HPA is able to convert isobutane directly into the aldehyde and acid with a selectivity of respectively 35 and 40% at an isobutane conversion of 10% [10]. The only disadvantage of these compounds is their rather low structure stability at elevated temperatures. On the other hand, several catalytic systems based on mixed oxides have been described for the partial oxidation of propane [11–23]. In the tracks of the oxyfunctionalization of propane, analogous materials have been tested for the partial oxidation of isobutane. Shishido et al. [24] describe a Mo–V–Sb catalyst which converts isobutane into methacrolein and isobutene with a selectivity of 27.6 and 12.5%, respectively, at an isobutane conversion of 8.1%. Iwasawa and co-workers [25,26] have studied new interesting catalysts (Pt/SbO_x) for the selective oxidation of isobutene and isobutane to methacrolein. Despite the efforts in R&D, the discovery of other new catalysts has progressed quite slowly. It is not clear whether this is due to conservative research planning or whether there are no better materials. Since intuitively the latter appears less likely, it was of interest to apply combinatorial approaches to search for new catalysts

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in this timely research area. Combinatorial techniques have received increasing attention [27,28] for the search of new materials and catalysts [29]. One of the problems associated with such a study is the availability of a catalyst synthesis protocol [30], which allows automated catalyst preparation within a wide range of compositional variations. This is, for example, not the case with most of the catalyst preparation protocols published [2–26]. Until now, the combinatorial search for new selective gas-phase oxidation catalysts has mainly been focused on the dehydrogenation of ethane and partial oxidation of propane [31–37].

In this paper the optimization of the Mo–V–Sb system for the partial oxidation of isobutane is described for the first time using a high-throughput MS screening setup, developed by Maier and co-workers [38,39]. Conventional experiments have been used to confirm that these new highly selective catalysts offer a better performance compared with the reference catalyst. Additionally, high-throughput screening based on an antimony-rich matrix has led to new catalytic systems.

2. Experimental and methods

The general strategy for rapid primary screening involved the creation of a library of spatially separated catalysts. Typically, 200 catalyst compositions were measured per experiment in the primary screening. The “library design” chosen consisted of four times 50 transparent HPLC glass flasks (2 ml) arranged in an addressable rack of 10 rows and five columns. The potential catalysts were synthesized directly in the HPLC flasks by means of an automated solution dispensing robot (LISSY, Zinsser Analytic).

For the synthesis, a modified acid-catalyzed sol–gel procedure

$$xM_1(OR_1)_k + yM_2(OR_2)_l + zM_3(OR_3)_m + 0.20H^+ + 65\text{solvent} \rightarrow \text{mixed oxides} \quad (1)$$

was applied, based on the synthesis procedure for amorphous mixed oxides [30,40], which lend themselves well to the use of dispensing robots.

Metal alkoxide precursor solutions (0.5 M) were prepared by dissolving commercially available metal alkoxides (vanadium (V) triisopropoxide, molybdenum (V) isopropoxide 5% w/v in isopropanol, tin (IV) isopropoxide, cobalt (II) propionate, copper (II) isopropoxide, nickel (II) propionate, cerium (IV) methoxide 18–20% w/v in methoxyethanol, titanium (IV) isopropoxide, aluminum *sec*-butoxide, zirconium (IV) *n*-propoxide 70% w/v in *n*-propanol, lanthanum (III) isopropoxide, chromium (III) isopropoxide 10–12% in isopropanol, iron (III) ethoxide 18–20% in ethanol, tantalum (V) ethoxide, manganese (II) propionate, bismuth 2-ethylhexanoate) or anhydrous metal chlorides (antimony (V) chloride, tellurium (IV) chloride, and niobium (V) chloride) in isopropanol. In the case of the metal chlorides in isopropanol, the solutions were flushed with argon in order to remove the formed HCl vapors. Proton acidity originated from a 0.15 M acetic acid solution in isopropanol.

The synthesis of the combinatorial catalyst libraries was drastically accelerated by the use of the library design software Plattenbau from Scheidtmann et al. [41]. A total amount of reagents of 250 µmol per flask was chosen. After adding all the reagents to each flask in a rack, the HPLC rack was covered and placed on an orbital shaker (Heidolph Titramax 100) for 45 min in order to obtain a homogeneous solution. These four racks were kept covered overnight in order to allow gel formation after which the lid was removed and the rack was placed under the hood for 3 days in order to allow the catalysts to dry. The resulting gels were calcined at 250 °C for 5 h (heating rate 0.5 °C per min) and at 400 °C for 8 h (heating rate 0.5 °C per min). The obtained powders were milled in the HPLC flasks and ≈ 50 mg was manually transferred to a 207-member steel library plate. Some wells were left empty for background comparison and one was filled with a reference catalyst for comparison. After a first screening run, the library was calcined again at 350 °C for 4 h (heating rate 2.5 °C per min) and at 600 °C for 6 h (heating rate 2.5 °C per min) in order to observe the effect of calcination temperature on the activity of the catalysts.

The same sol–gel procedure was used for the large scale sol–gel synthesis. Typically, 100 ml of a 0.5 M $SbCl_5$ solution in isopropanol was prepared by adding $SbCl_5$ in small amounts to the isopropanol while flushing the solution with argon. Then, 2.222 ml of a 0.5 M vanadium (V) triisopropoxide solution in isopropanol and 44.444 ml of a 0.1 M molybdenum (V) isopropoxide solution in isopropanol were added to this solution. After addition of 70 ml of isopropanol the solution was stirred for 15 min. Afterward, 100 ml of a 0.15 M acetic acid solution in isopropanol was added to the solution obtained and stirred for another 45 min. Gel formation occurred overnight in a closed vessel. To allow drying, the gel was poured in a petri plate and placed uncovered in the hood for 3 days. For calcination of the powders, the same procedure was used as described above.

The reference catalyst used was synthesized following the slurry procedure of Shishido et al. [24]. Sb_2O_3 was dispersed in an oxalic acid aqueous solution, to which a hot aqueous solution of NH_4VO_3 and $(NH_4)_3Mo_7O_{24} \cdot 4H_2O$ was added. The mixture was heated under reflux conditions at 90 °C for 24 h. The precipitate was dried from the solution by evaporation of the solvent first at 80 °C and then at 100 °C for 15 h. It was grinded into a fine powder and calcined at 350 °C for 4 h and finally at 600 °C for 6 h in air. The slurry-type catalyst showed the following composition: $Mo_{8.3}V_{8.3}Sb_{83.3}$.

High-throughput screening of the catalysts was performed using spatially resolved mass spectrometry [38,39]. A capillary bundle containing both the educt gas supply and the product gas sampling system was then inserted sequentially into each reaction chamber of the library plate. The movement of the latter was provided by an xyz stage, while the position of the capillary bundle remained unchanged (Fig. 1). The flow of the experiment was controlled by the

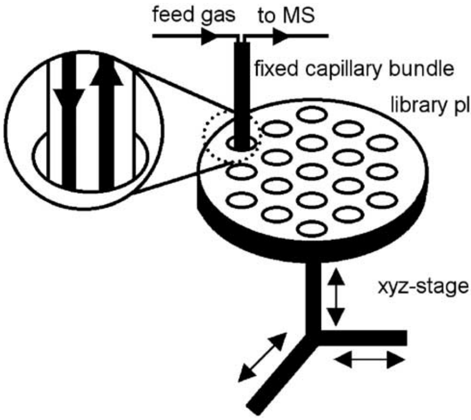

Fig. 1. Scheme of the high-throughput screening reactor using spatially resolved mass spectrometry.

software TestRig [39]. At a total feed flow of 5 ml min^{-1}, an isobutane/oxygen/helium gas mixture with volumetric composition of 15/5/10 was continuously fed to the capillary bundle using calibrated mass flow controllers. A Balzers QMA 125 mass spectrometer with Quadstar software was used. The product formation for each catalyst was monitored sequentially for 65 s under isothermal conditions (400 °C). The whole high-throughput screening (including heating up, pretreatment of the library in situ at 410 °C in air for 2 h) of one library with 200 catalysts was completed in approximately 8 h. The detection through MS was performed by recording ion currents of the following ions ($F =$ Faraday mode, $C =$ Channeltron mode): $m/z = 36$ (argon, C), $m/z = 40$ (argon, F), $m/z = 44$ (CO_2, F), $m/z = 43$ (isobutane, F), $m/z = 56$ (isobutene, C), $m/z = 70$ (methacrolein, C), and $m/z = 86$ (methacrylic acid, C). The ion $m/z = 28$ for CO was not used because of interference with fragmentation ions from CO_2 and isobutene.

Data evaluation was done using published software [42]. The raw MS data were first averaged using 3 values for each catalyst and each selected m/z, the scans of interest being normalized with respect to the argon signal ($m/z = 36$). In this way the relative performance of each catalyst could be compared to that of the reference catalyst, set to 100%.

Conventional tests were carried out in a gas-phase tubular flow quartz reactor between 325 and 450 °C at atmospheric pressure. Catalyst (2.0 g), pelletized to a 0.125–0.250-mm fraction and diluted with 1.0 g of SiC of the same granule size, was packed between two layers of quartz wool. The same feed composition was used described in the primary screening, but with a total flow rate of 40 ml min^{-1} ($\mathrm{GHSV} = 900\ \mathrm{ml\,h^{-1}\,g_{cat}^{-1}}$). The sol–gel catalysts calcined at 400 °C were activated in situ prior to reaction at 400 °C in a flow of 20% oxygen in helium for 2 h, whereas the ones calcined at 600 °C were activated at 500 °C in a flow of 20% oxygen in helium for 2 h. Feed and products were analyzed with an on-line HP 5890 series II gas chromatograph equipped with (i) a CP WCOT fused silica column connected to a methanizer and an FID, and (ii) a molecular sieve 5 Å column connected to a TCD.

The conventionally synthesized catalysts were characterized using XRD, IR, and Raman spectroscopy. The XRD characterization was carried out at room temperature using a D5000 Siemens X-ray diffractometer equipped with a Cu-K_α source. Infrared spectra were recorded on a Nicolet 730 FTIR spectrometer, using the KBr wafer technique. Laser Raman spectra were collected with an FRA 106/S Brüker instrument at room temperature. The power of the laser source was adjusted to 250 mW in defocused mode with a wavelength of 1064 nm.

3. Results and discussion

3.1. High-throughput screening

In order to be able to rapidly screen the catalytic activity of modified Sb oxides including wide compositional variations, and high-throughput approaches, the availability of suitable recipes for catalyst preparation is a prerequisite. Therefore, a sol–gel recipe has been selected, that allowed the intended compositional variation [30]. The material obtained after gelation, drying, and calcinations was highly amorphous and therefore structurally significantly different from conventionally prepared catalysts. Once the catalytic activity/selectivity of such materials was confirmed under conventional reaction conditions, combinatorial tests could be planned.

As a starting point an exploration of the composition space of the ternary mixed oxides of MoVSb was chosen. Instead of attempting to optimize the known composition of active Mo–V–Sb catalysts from the literature, a spread of the composition library was prepared, where Sb was allowed to vary between 80 and 100 mol%, while Mo and V were changed between 0 and 20 mol%, in steps of 2 mol%. Such a spread of composition libraries has the advantage that the whole composition space is explored and local maxima, if present, are identified. In addition, the reference catalyst was placed on all libraries for comparison.

3.1.1. $Mo_{0–20}V_{0–20}Sb_{80–100}$ oxides

The spread of composition library of the mixed oxides of $Mo_{0–20}V_{0–20}Sb_{80–100}$ was planned with the help of the Plattenbau software. Catalyst synthesis, transfer to the library plate, pretreatment, reaction at 400 °C, and data treatment were described in the experimental section. Catalyst performance is associated with the relative intensity of the averaged and normalized signals of $m/z = 70$ for methacrolein, $m/z = 56$ for isobutene, and $m/z = 44$ for CO_2 and compared to that of the reference catalyst.

Fig. 2 summarizes the catalytic performance against the compositional spread of the ternary mixed oxides of Mo–V–Sb. The highest activity for methacrolein formation from isobutane is found at a ridge with 2 mol% V in the range

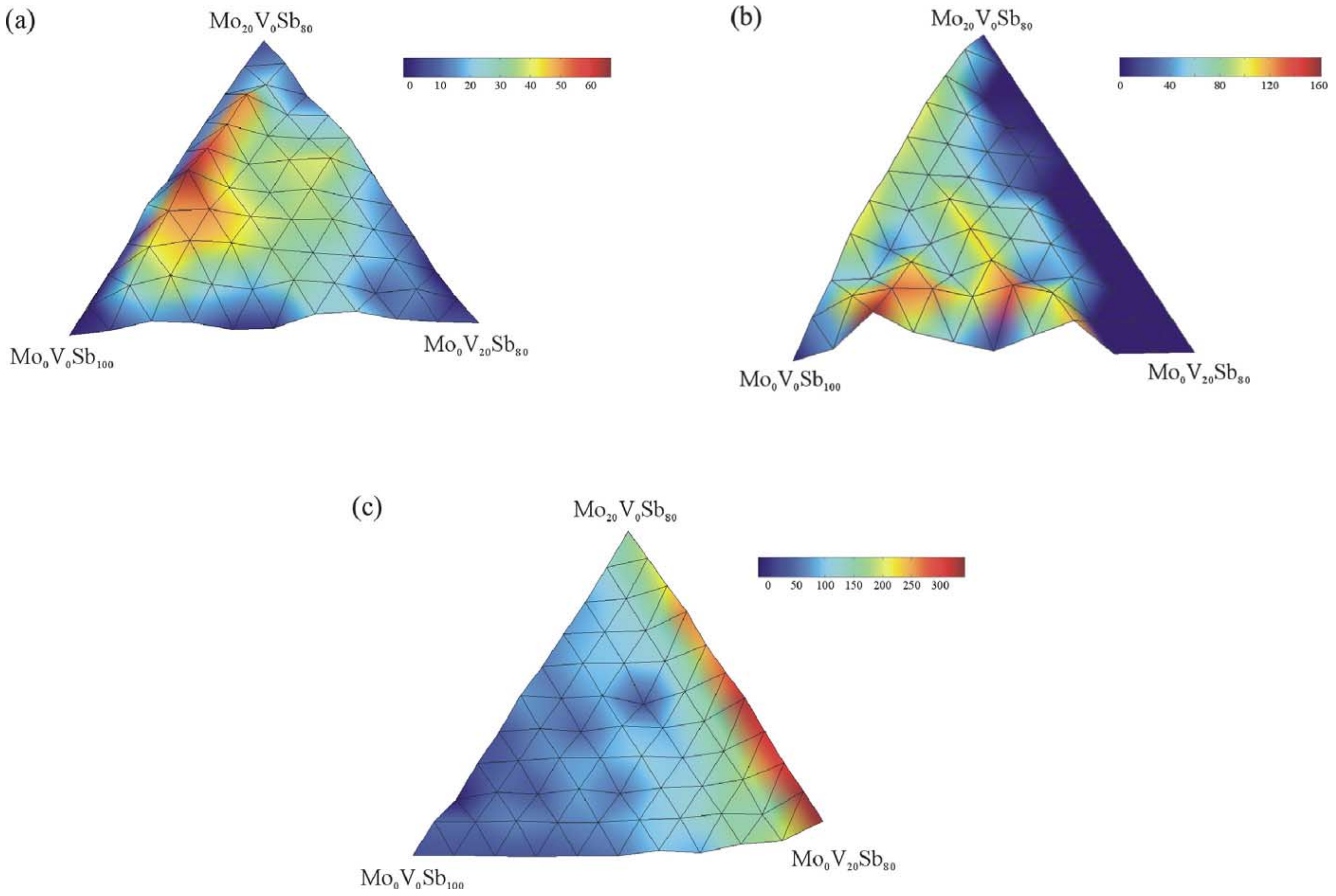

Fig. 2. Relative isobutane conversion (%) to (a) methacrolein, (b) isobutene, (c) CO_2 for a combinatorial library consisting of sol–gel-synthesized mixed-metal oxides with 0–20% molybdenum, 0–20% vanadium, and 80–100% antimony in 2% increments, and calcined at 400 °C, compared to a literature MoVSb slurry-type catalyst.

of 6–14 mol% Mo (Fig. 2a). The most active catalyst is $Mo_8V_2Sb_{90}$, which shows 65% of the activity of the reference catalyst on the library for aldehyde formation. The highest dehydrogenation activity is found in another region of composition with low Mo content and higher V content (Fig. 2b). Fig. 2c shows, that the CO_2 production was relatively low for all these compositions, total oxidation being located in the region lowest in Sb and higher in V. Whereas the binary $Mo_{0–20}Sb_{80–100}$ catalysts formed only little methacrolein, the presence of a small amount of vanadium dramatically increased both activity and selectivity toward the aldehyde. For all catalysts, the formation of methacrylic acid was negligible.

Calcination of the same library at 600 °C resulted in a gradual increase of the relative formation of isobutene, methacrolein, and CO_2 of all the sol–gel-synthesized catalysts. Particularly, for the $Mo_8V_2Sb_{90}$ sample the relative performance toward the aldehyde and CO_2 was 2.5 times higher compared to the same sample calcined at 400 °C, whereas the isobutene content increased only slightly (Fig. 3). The selectivity to the aldehyde was now much better than that of the reference catalyst. $Mo_8V_2Sb_{90}$ was the best methacrolein-forming catalyst at both temperatures.

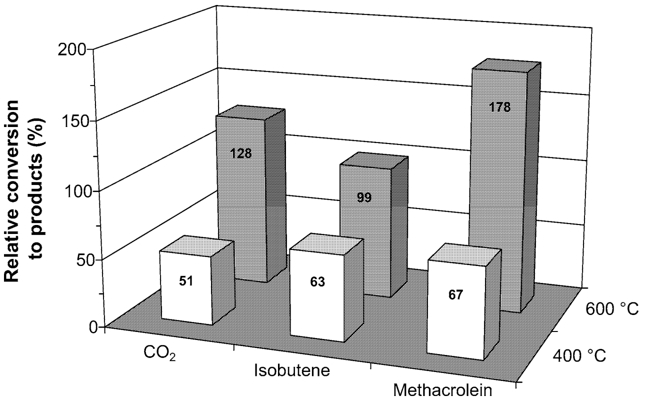

Fig. 3. Effect of the calcination temperature on the relative isobutane conversion to methacrolein, isobutene, and CO_2 of the $Mo_8V_2Sb_{90}$ sample in the Mo–V–Sb combinatorial library. The slurry-type reference catalyst was $Mo_{8.3}V_{8.3}Sb_{83.3}$.

3.1.2. $M_xM^*_{10-x}Sb_{90}$ oxides

In a search for other active elements, a number of other elements were used as dopant in the standard MoVSb library. The compositions of the samples was chosen in the $M_xM^*_{10-x}Sb_{90}$ region, where x varied from 0, 2, 4, 6, 8, to 10. Two libraries were synthesized with binary combi-

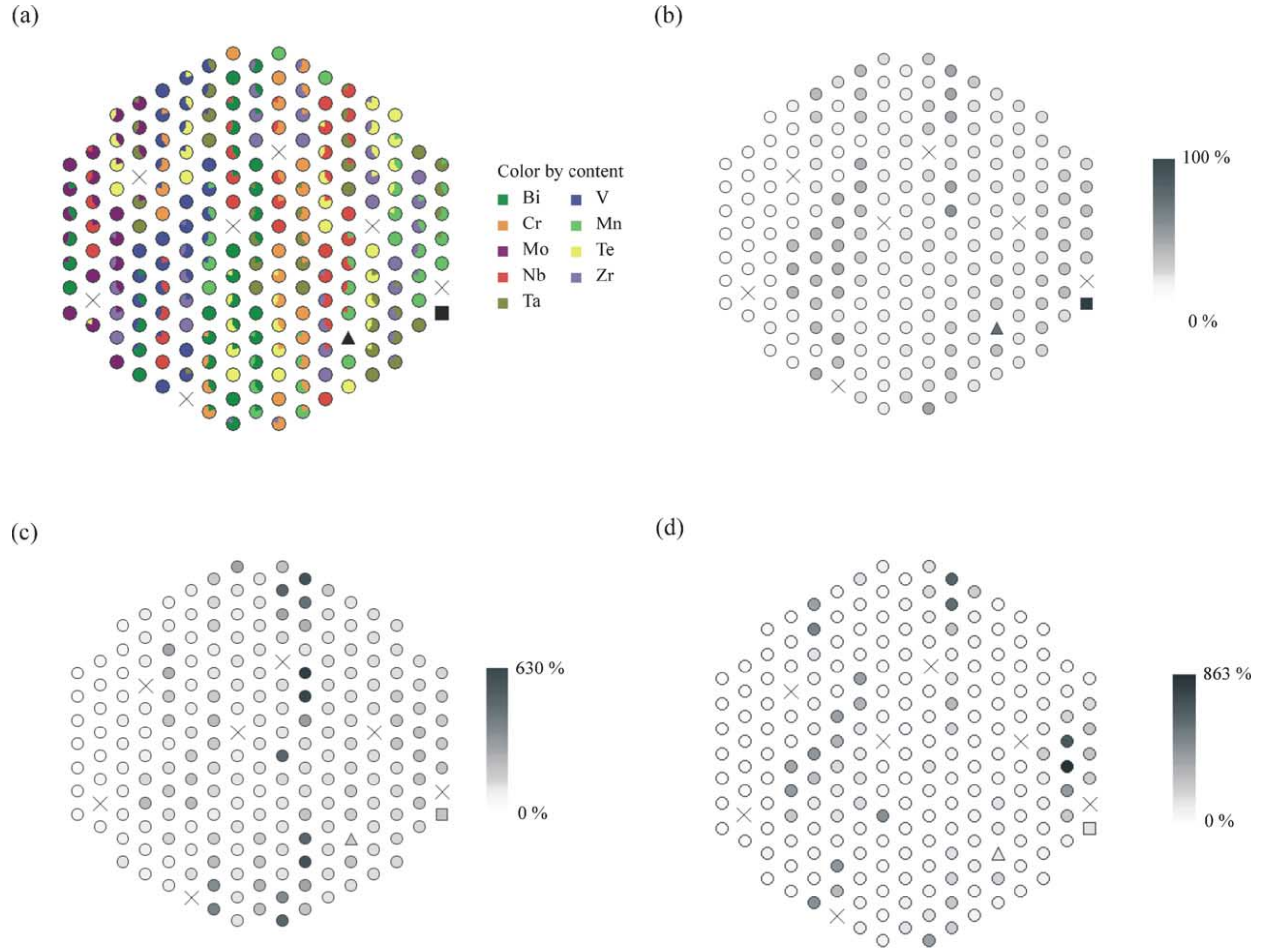

Fig. 4. Library construction of sol–gel-synthesized mixed-metal oxides in the $M_xM^*_{10-x}Sb_{90}$ region (a), where M and M* correspond to the combinations given in Table 1. Relative isobutane conversion (%) to (b) methacrolein, (c) isobutene, (d) CO_2 for this library calcined at 400 °C (□, reference catalyst; ▲, $Mo_8V_2Sb_{90}$; ×, blank).

nations of the following elements (M and M*): Mo, V, Bi, Cr, Nb, Te, Zr, Ta, Mn and Sn, Fe, Cu, Ni, Ce, Ti, Al, Co, La, as given in Tables 1 and 2, and calcined at 400 °C. For each library this resulted in $33 \times 6 = 198$ samples. In both libraries the best catalyst found above, $Mo_8V_2Sb_{90}$, was added as well as the reference catalyst in order to allow for comparison (Figs. 4a and 5a). None of the catalysts showed higher aldehyde production compared to the reference catalyst, but several samples showed improved isobutene formation (Figs. 4b and c and 5b and c). The samples in the first library (Fig. 4), active for dehydrogenation, corresponded to vanadium and chromium-doped oxides. For the second library (Fig. 5), iron-containing oxides produced the highest amount of methacrolein, though the relative per-

Table 1
Combinations of 2 different elements (M and M*) from a group of 9 elements for the library design in the $M_xM^*_{10-x}Sb_{90}$ compositional space

	Mo	V	Bi	Cr	Nb	Te	Zr	Ta	Mn
Mo	■								
V	▨	■							
Bi	1	6	■						
Cr	▨	7	13	■					
Nb	2	8	14	19	■				
Te	3	9	15	20	24	■			
Zr	4	10	16	21	25	28	■		
Ta	5	11	17	22	26	29	31	■	
Mn	▨	12	18	23	27	30	32	33	■

The numbers given only count the binary systems prepared.

Table 2
Combinations of 2 different elements (M and M*) from a group of 9 elements for the library design in the $M_xM^*_{10-x}Sb_{90}$ compositional space

	Sn	Fe	Cu	Ni	Ce	Ti	Al	Co	La
Sn	■								
Fe	1	■							
Cu	2	9	■						
Ni	3	10	16	■					
Ce	4	11	17	22	■				
Ti	5	12	18	23	27	■			
Al	6	13	19	24	28	31	■		
Co	7	14	20	25	29	32	33	■	
La	8	15	21	26	30	▨	▨	▨	■

The numbers given only count the binary systems prepared.

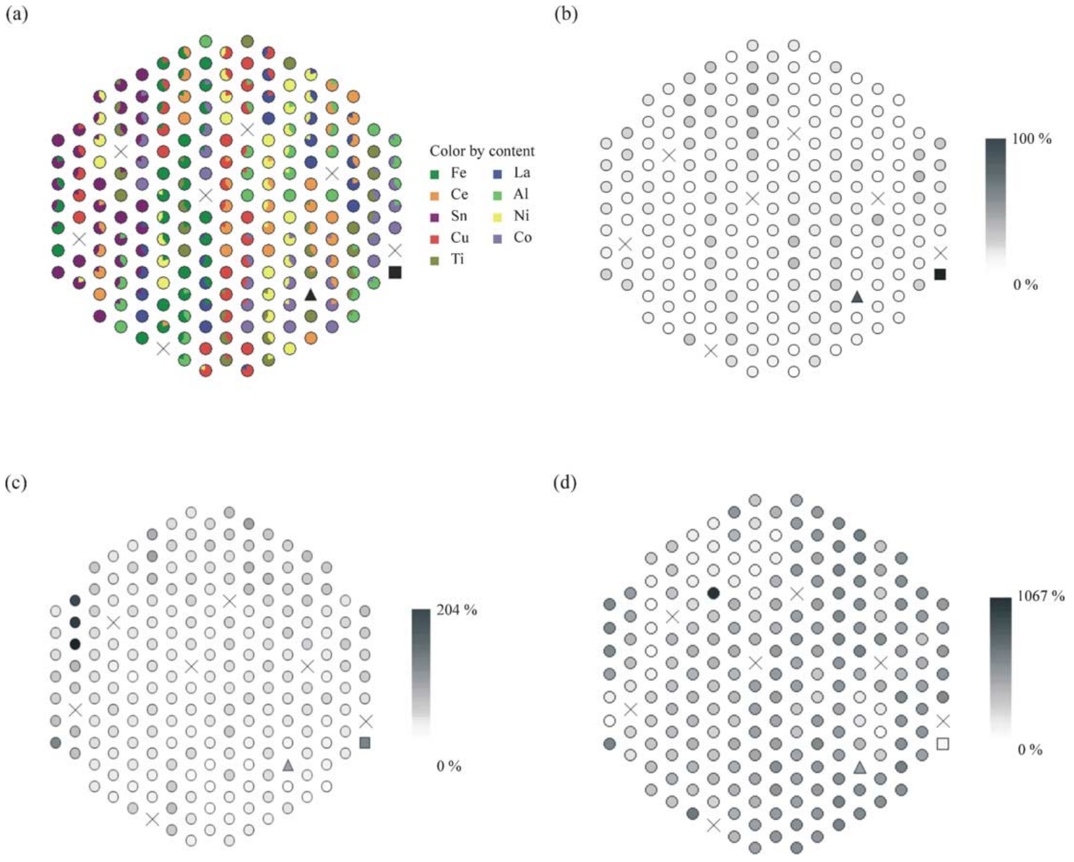

Fig. 5. Library construction of sol–gel-synthesized mixed-metal oxides in the $M_xM^*_{10-x}Sb_{90}$ region (a), where M and M* correspond to the combinations given in Table 2. Relative isobutane conversion (%) to (b) methacrolein, (c) isobutene, (d) CO_2 for this library calcined at 400 °C (□, reference catalyst; ▲, $Mo_8V_2Sb_{90}$; ×, blank).

formance was still lower than that of the reference catalyst. In general, the materials of both libraries produced significantly more CO_2 than the $Mo_{0–20}V_{0–20}Sb_{80–100}$ oxides, although, as before, there is no correlation between among oxidation, dehydrogenation and combustion activity (Figs. 4d and 5d).

In contrast to the behavior of the $Mo_{0–20}V_{0–20}Sb_{80–100}$ oxides, calcination of both libraries at 600 °C did not improve the aldehyde formation activity of these new catalysts. It was interesting to note, that among all the binary modifiers of Sb oxide studied, the well known Mo–V remained the most active and selective one for methacrolein formation.

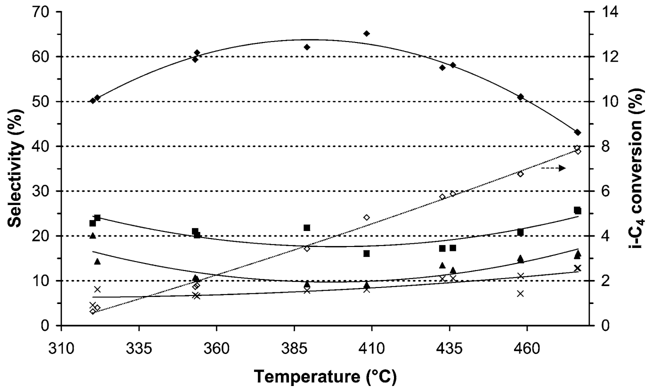

Fig. 6. Conversion/selectivity vs reaction temperature for isobutane oxidation with reference catalyst (■, methacrolein; ▲, isobutene; ◆, CO_x (= CO_2 + CO); ◇, isobutane; ×, propane and propene), measured via conventional testing in a single-bed continuous flow microreactor. Arrows compare initial activity on a given temperature to steady activity (after 1 h).

3.2. Conventional testing

3.2.1. Reference catalyst

In a first experiment the performance of the reference catalyst $Mo_{8.3}V_{8.3}Sb_{83.3}$, prepared according to the literature [24], was studied as a function of the reaction temperature (Fig. 6). The reference catalyst showed the highest methacrolein selectivity (25.8%) at a conversion of 7.9% and at a reaction temperature of 475 °C. The selectivity toward CO_x (45–65%) was rather high for the reference catalyst in this temperature range. These results correspond with the reported results in the literature [24].

When the reaction was carried out at 450 °C in the absence of catalyst, the isobutane conversion was less than 0.5%, indicating that the effect of homogeneous gas-phase radical reactions below this temperature can be neglected.

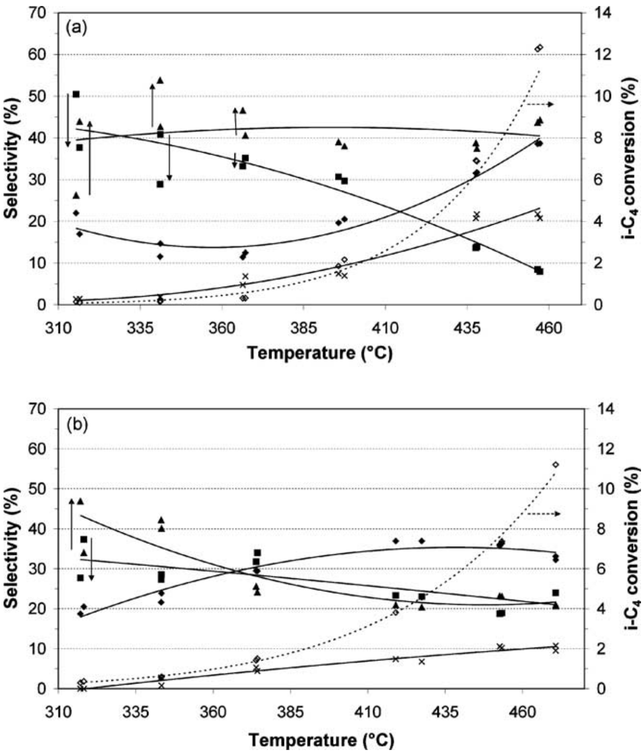

Fig. 7. Conversion/selectivity vs reaction temperature for isobutane oxidation for the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalyst calcined at (a) 400 °C and (b) 600 °C (symbols as in Fig. 6).

3.2.2. $Mo_8V_2Sb_{90}$

Fig. 7a shows the catalytic performance against reaction temperature for isobutane oxidation of $Mo_8V_2Sb_{90}$, synthesized through the sol–gel procedure and calcined at 400 °C. The conversion of isobutane increased with increasing reaction temperature. The selectivity to methacrolein decreased from the initial 50% at a temperature of 315 °C to 38% over a period of 1 h. On the other hand, the selectivity to isobutene simultaneously increased at that temperature. By increasing the reaction temperature the methacrolein selectivity decreased, while the isobutene selectivity remained approximately the same. The selectivity toward CO_x $(= CO_2 + CO)$ was dramatically lower compared with the reference catalyst over the temperature range tested, and remained under 20% for temperatures below 400 °C.

Whereas the $Mo_8V_2Sb_{90}$ sol–gel catalyst, calcined at 600 °C (Fig. 7b), showed lower initial selectivity to methacrolein, the selectivity drop with increasing reaction temperature was less pronounced compared to the catalyst calcined at 400 °C. The conversion of isobutane followed a similar trend, but was systematically lower at reaction temperatures below 420 °C. On the other hand a lower isobutene and higher CO_x selectivity was observed over the whole reaction temperature range tested. These results confirm the data obtained in the combinatorial screening noted in Fig. 2.

The effect of time on stream of the sol–gel $Mo_8V_2Sb_{90}$ catalyst, calcined at 400 °C, on the product distribution in the oxidation of isobutane at 365 °C is presented in Fig. 8a.

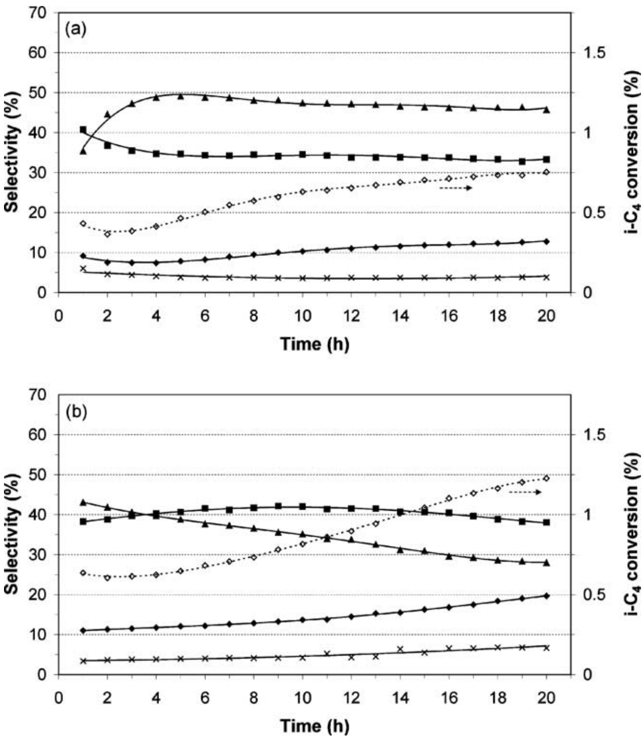

Fig. 8. Conversion/selectivity vs time on stream for isobutane oxidation for the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalyst calcined at (a) 400 °C and (b) 600 °C (symbols as in Fig. 6).

Initially, a decrease in methacrolein selectivity of 6% could be observed during a period of 5 h, after which the selectivity toward the aldehyde is stabilized. At the same time, a steep increase in isobutene selectivity was observed, after which a slight decrease occurred. This slight decrease was compensated by a small increase in CO_x formation. After 20 h on stream, the isobutane conversion was doubled compared to the initial activity. The same catalyst, calcined at 600 °C, showed a different conversion/selectivity behavior with time on stream (Fig. 8b). The initial isobutane conversion was almost twice as high, compared with the sample calcined at 400 °C, and increased in the same manner to a value twice as high. The initial selectivity toward methacrolein was equal to the one obtained for the sample calcined at 400 °C, but remarkably, this value did not decrease with time on stream. On the other hand, the initial selectivity to isobutene was higher, but exhibited a continuously decreasing behavior. This decrease was mainly compensated by an increase of CO_x selectivity, which was higher compared to the sample calcined at 400 °C.

Fig. 9a shows the effect of the gas hourly space velocity (GHSV) on the catalytic performance of the sol–gel-synthesized $Mo_8V_2Sb_{90}$ sample calcined at 400 °C. The temperature of the catalyst was kept at 365 °C. By reducing the GHSV 900 to 450 $\mathrm{ml\,h^{-1}\,g_{cat}^{-1}}$, the conversion of isobutane could be doubled without loss of aldehyde selectivity. The loss of isobutene selectivity was again mainly compensated by an increase of CO_2 production. For the sol–gel synthesized sample calcined at 600 °C (Fig. 9b), a similar trend

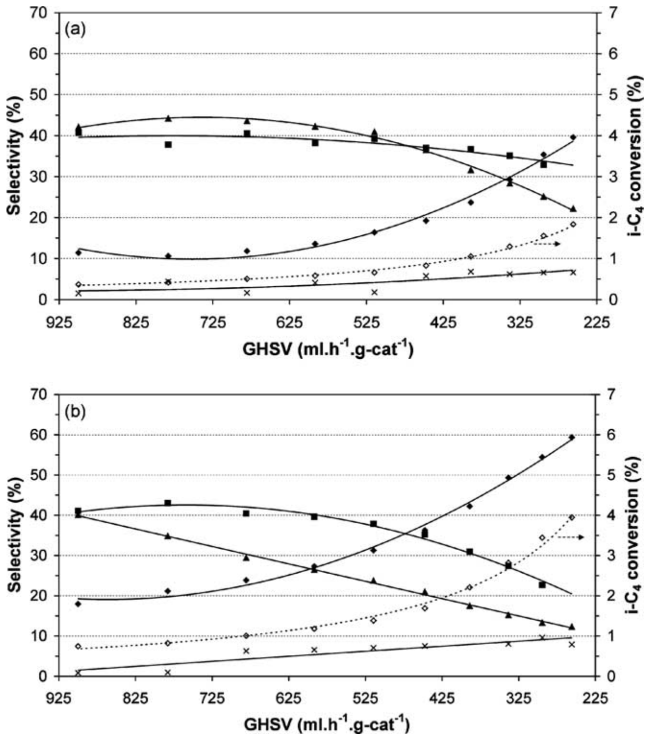

Fig. 9. Effect of the linearly space velocity (GHSV) for isobutane oxidation for the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalyst calcined at (a) 400 °C and (b) 600 °C (symbols as in Fig. 6).

for the aldehyde selectivity was observed, but the isobutane conversion was twice that of the sample calcined at 400 °C. The selectivity toward CO_2 was also higher, resulting in a lower isobutene selectivity.

3.2.3. $Mo_{8.3}V_{8.3}Sb_{83.3}$

In order to examine whether the optimized catalyst composition is more active than the reference catalyst and to compare the sol–gel catalysts of the same composition to the reference catalyst, a mixed oxide of composition $Mo_{8.3}V_{8.3}Sb_{83.3}$ was prepared by the sol–gel method. Fig. 10 shows the catalytic performance in the oxidation of isobutane against the reaction temperature. The conversion of isobutane increased with increasing reaction temperature, similarly to the $Mo_8V_2Sb_{90}$ catalyst. The initial selectivity to methacrolein was much lower than that of the $Mo_8V_2Sb_{90}$ catalyst, but approached the same value of 25% at 375 °C. On the other hand, the initial selectivity toward CO_x was much higher compared to the optimized catalyst composition and much lower than that of the reference catalyst at lower temperatures, it increased up to 50% with increasing reaction temperature. Overall, the performance of this catalyst for selective methacrolein formation was inferior to that of the best catalyst, and slightly superior to that of the reference catalyst. This confirms the results obtained in the combinatorial study and shows that the simple sol–gel recipe produces catalysts of activity and selectivity comparable or better than the conventional preparation procedure. At the same time, the isobutene selectivity decreased with increasing temperature.

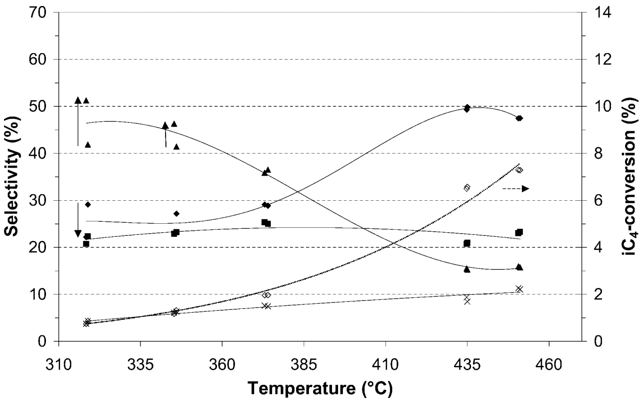

Fig. 10. Conversion/selectivity vs reaction temperature for isobutane oxidation for the sol–gel-synthesized $Mo_{8.3}V_{8.3}Sb_{83.3}$ catalyst calcined at 400 °C (symbols as in Fig. 6).

3.3. Characterization of the Mo–V–Sb mixed oxides

X-ray powder diffraction of the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalyst, calcined at 400 °C, at best showed only broad reflections, pointing to an amorphous structure as confirmed by TEM. For the catalyst with the same elemental composition, but calcined at 600 °C, several crystalline phases could be identified together with an amorphous structure (Fig. 11). The major phases were Sb_2O_5 (JCPDS 11-0690), Sb_6O_{13} (JCPDS 33-0111), and SbO_4 (JCPDS 36-1163). The diffraction peaks of the V_2O_5 and MoO_3 phases could not be observed in the $Mo_8V_2Sb_{90}$ sol–gel-synthesized catalysts, indicating that crystalline V_2O_5 and MoO_3 were absent in these catalysts.

The IR spectra of the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalysts and the reference catalyst are seen in Fig. 12. The IR spectrum for the sol–gel-synthesized sample, calcined at 400 °C, showed three broad bands at 440, 555, and 728 cm^{-1}, which could be assigned to the presence of the Sb_xO_y phases. The broadening in the bands is in line with the amorphous character of the sample. On the other hand,

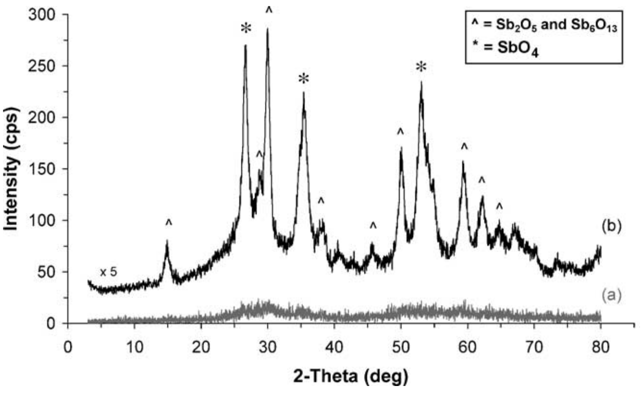

Fig. 11. XRD pattern of the $Mo_8V_2Sb_{90}$ sample, synthesized through the sol–gel procedure, and calcined at (a) 400 °C and (b) 600 °C under air.

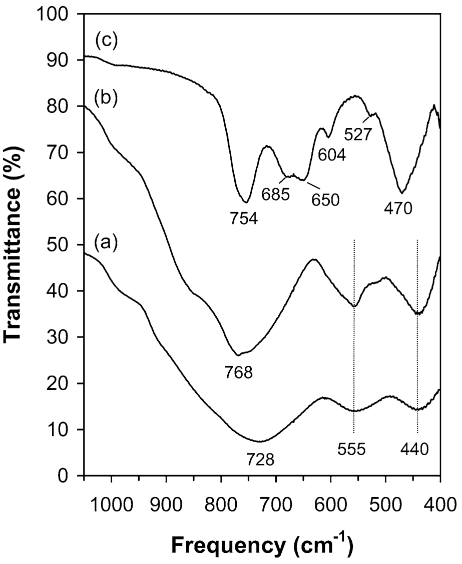

Fig. 12. Infrared spectra of the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalysts, calcined at (a) 400 °C and (b) 600 °C and (c) the reference catalyst.

for the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalyst, calcined at 600 °C, sharper bands were obtained, shifted to higher frequencies, probably due to the presence of crystalline regions and small changes in chemical environment. The IR spectrum of the reference catalyst corresponded mainly to the presence of an α-Sb_2O_4 phase [42].

The Raman spectrum for the reference catalyst (Fig. 13c) showed three well-defined bands at 865, 400, and 198 cm^{-1}, which could be assigned to α-Sb_2O_4 [24].

In the Raman spectra for the sol–gel-synthesized $Mo_8V_2Sb_{90}$ samples, calcined at 400 °C and 600 °C (Fig. 13a and b, respectively) four strong bands appeared at 960–980, 870-895, 630–660, and 460 cm^{-1}. According to Desikan et al. [47], these bands arise from Mo–O–Mo bonds and Mo=O stretching. The bands at 461 and 198 cm^{-1} are associated with the presence of Sb_xO_y phases. Consistent with the data obtained by XRD, no crystalline V_2O_5 or MoO_3 could be found in the three Raman spectra [43–47].

4. Conclusions

Combinatorial methodologies encompassing all synthetic and screening steps have been used to screen antimony-rich mixed-oxide catalysts for the selective oxidation of isobutane. An acid-catalysed sol–gel procedure was used for the high-throughput synthesis of these mixed metal-oxide library compositions. By the use of spatially resolved mass spectrometry, the optimal composition toward aldehyde formation has been determined rapidly in an automated fashion. The availability of library design software, robot synthesis of libraries, and rapid screening and data analysis by software allowed us to conduct the whole combinatorial study within 2 months.

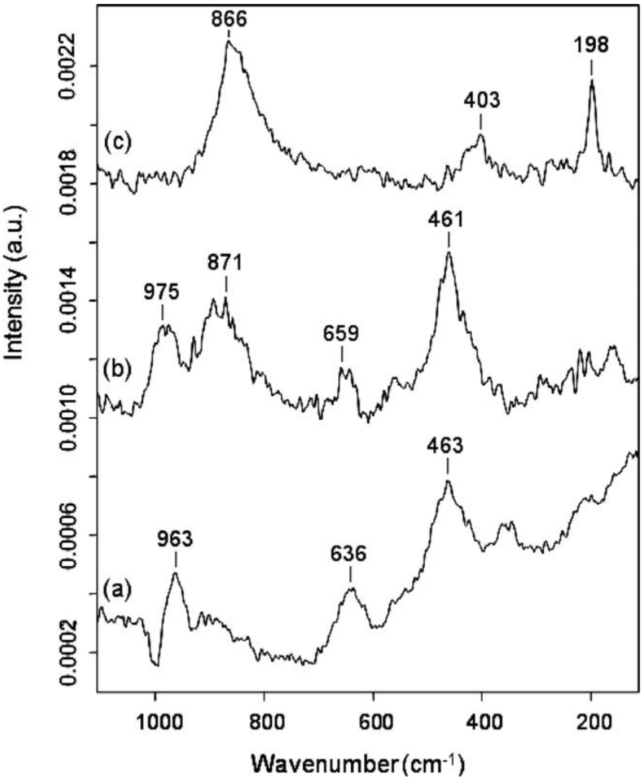

Fig. 13. Raman spectra of the reference catalyst, and the sol–gel-synthesized $Mo_8V_2Sb_{90}$ catalysts, calcined at 400 and 600 °C.

First, the optimal composition of the Mo–V–Sb system was identified using a composition-spread approach sampling the complete $Mo_{0–20\%}V_{0–20\%}Sb_{80–100\%}$ compositional space. The optimal composition, $Mo_8V_2Sb_{90}$, showed an improved performance compared to the best literature reference catalyst.

Scale-up of the preparation of the optimal catalyst composition and testing in a conventional gas-phase flow reactor confirmed the results of the screening experiments. In addition, other libraries of antimony-rich oxides doped with a higher number of elements where prepared and tested by high throughput methods. None of these new mixed oxides, however, could match the unique performance of the new Mo–V–Sb catalyst for the selective oxidation of isobutane to methacrolein.

Physicochemical characterization of the libraries calcined at 400 °C showed essentially amorphous catalysts. The use of enhanced calcination temperatures, however, the appearance of crystalline phases in the catalysts, and the enhancement of the catalytic properties pointed the importance of composition and calcinations temperature as crucial catalyst preparation parameters.

The study has demonstrated the power of the combinatorial approach, especially for the mapping out of compositional hyperspaces and the identification of local performance maxima.

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References

[1] R.K. Grasselli, Top. Catal. 21 (2002) 79.
[2] N. Yoshihiko, O. Motomasa, N. Koichi, S. Hiroshi, Eur. patent 0418657 A2, 1990.
[3] Y. Setsuo, Y. Tatsuo, US patent 5,191,116, 1993.
[4] K. Yuichi, O. Hideo, US patent 6476259 B2, 2001.
[5] M. Misono, N. Mizuno, K. Inumaru, G. Koyano, X.-H. Lu, Stud. Surf. Sci. Catal. 110 (1997) 118.
[6] K. Inumaru, A. Ono, H. Kubo, M. Misono, J. Chem. Soc., Faraday Trans. 94 (1998) 1765.
[7] N. Mizuno, H. Yahiro, J. Phys. Chem. B 102 (1998) 437.
[8] M. Langpape, J.M. Millet, U.S. Ozkan, P. Delichere, J. Catal. 182 (1999) 148.
[9] M. Misono, Top. Catal. 21 (2002) 89.
[10] W. Li, W. Ueda, in: Proc., 3rd World Congress on Oxidation Catalysis, 1997, p. 433.
[11] Mitsubishi Chemical Corporation, Jpn. patent 10045664-A, 1996.
[12] M. Lin, M.W. Linsen, Eur. patent 0962253-A3, 1999.
[13] M. Takahashi, X. Tu, T. Hirose, M. Ishii, US patent 5,994,580, 1999.
[14] G. Centi, P. Mazzoli, S. Perathoner, Appl. Catal. A 165 (1997) 273.
[15] A.C. Kaddouri, C. Mazzocchia, E. Tempesti, Appl. Catal. A 180 (1999) 271.
[16] H. Watanabe, Y. Koyasu, Appl. Catal. A 194–195 (2000) 479.
[17] M. Lin, T.B. Desai, F.W. Kaiser, P.D. Klugherz, Catal. Today 61 (2000) 223.
[18] W. Ueda, K. Oshihara, Appl. Catal. A 200 (2000) 135.
[19] S.A. Holmes, J. Al-Saeedi, V.V. Guliants, P. Boolchand, D. Georgiev, U. Hackler, E. Sobkow, Catal. Today 67 (2001) 403.
[20] P. Botella, B. Solsona, A. Martinez-Arias, J.M. López Nieto, Catal. Lett. 74 (2001) 149.
[21] J.N. Al-Saeedi, V.V. Guliants, Appl. Catal. A 237 (2002) 111.
[22] E.K. Novakova, J.C. Védrine, E.G. Derouane, J. Catal. 211 (2002) 226.
[23] E.K. Novakova, J.C. Védrine, E.G. Derouane, J. Catal. 211 (2002) 235.
[24] T. Shishido, T. Inoue, I. Matsuura, K. Takehira, Catal. Lett. 68 (2000) 215.
[25] T. Inoue, K. Asakura, W. Li, S.T. Oyama, Y. Iwasawa, Appl. Catal. A 165 (1997) 183.
[26] T. Inoue, K. Asakura, Y. Iwasawa, J. Catal. 171 (1997) 457.
[27] J. Newsam, F. Schüth, Biotech. Bioeng. 61 (1999) 203.
[28] S. Senkan, Angew. Chem. Int. Ed. 40 (2001) 312.
[29] J. Scheidtmann, P.A. Weiß, W.F. Maier, Appl. Catal. A 222 (2001) 79.
[30] T. Wolter, PhD thesis, Saarbrücken, 2003.
[31] Y. Liu, P. Cong, R.D. Doolen, H.W. Turner, W.H. Weinberg, Catal. Today 61 (2000) 87.
[32] D. Wolf, O.V. Buyevskaya, M. Baerns, Appl. Catal. A 200 (2000) 63.
[33] A. Hagemeyer, B. Jandeliet, Y. Liu, D.M. Poojary, H.W. Turner, A.F. Volpe Jr., W.H. Weinberg, Appl. Catal. A 221 (2001) 23.
[34] M. Baerns, O.V. Buyevskaya, A. Brückner, E. Kondratenko, M. Langpape, D. Wolf, Stud. Surf. Sci. Catal. 140 (2001) 55.
[35] O.V. Buyevskaya, A. Brückner, E.V. Kondratenko, D. Wolf, M. Baerns, Catal. Today 67 (2001) 369.
[36] S.A. Holmes, J. Al-Saeedi, V.V. Guliants, P. Boolchand, D. Georgiev, U. Hackler, E. Sobkow, Catal. Today 67 (2001) 403.
[37] J.N. Al-Saeedi, V.V. Guliants, Appl. Catal. A 237 (2002) 111.
[38] M. Orschel, J. Klein, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 38 (1999) 2791.
[39] J. Urschey, P.-A.W. Weiss, J. Scheidtmann, R. Richter, W.F. Maier, Solid State Sci., in press.
[40] W.F. Maier, I.-C. Tilgner, M. Wiedorn, H.-C. Ko, Adv. Mater. 5 (1993) 726.
[41] J. Scheidtmann, J.W. Saalfrank, W.F. Maier, submitted for publication.
[42] D.J. Stewart, O. Knop, C. Ayasse, F.W.D. Woodhams, Can. J. Chem. 50 (1972) 690.
[43] P.-A.W. Weiss, J.W. Saalfrank, J. Scheidtmann, H.-W. Schmidt, W.F. Maier, in: E. Amis, R.A. Potyrailo (Eds.), High Throughput Analysis: A Tool for Combinatorial Materials Science, Kluwer Academic, Dordrecht, in press.
[44] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, Spectrochim. Acta A 39 (1983) 641.
[45] S.T. Oyama, G.T. Went, K.B. Lewis, A.T. Bell, G.A. Somorjai, J. Phys. Chem. 93 (1989) 6786.
[46] S. Takenaka, T. Tanaka, T. Yamazaki, T. Funabiki, S. Yoshida, J. Phys. Chem. B 101 (1997) 9035.
[47] A.N. Desikan, L. Huang, S.T. Oyama, J. Phys. Chem. 95 (1991) 10050.