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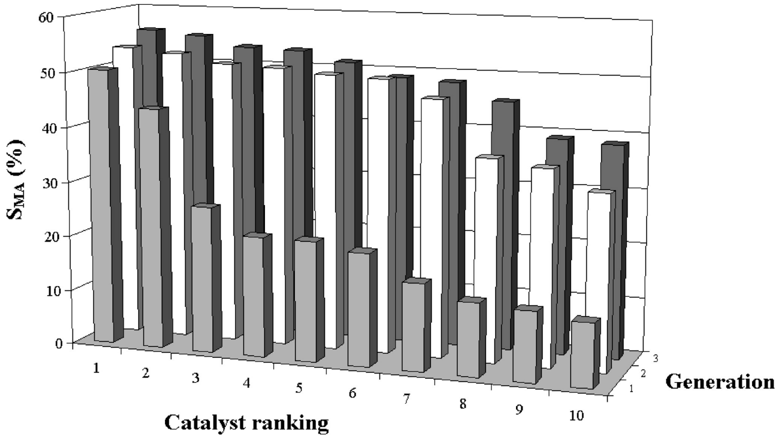

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Optimization of MoVSb Oxide Catalyst for Partial Oxidation of Isobutane by Combinatorial Approaches

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Optimization of the Mo−V−Sb mixed-oxide system for the selective oxidation of isobutane to methacrolein by true combinatorial methods primarily is intended to reduce the number of experiments in a broad parameter space. Therefore, an evolutionary approach based on a genetic algorithm has been chosen to screen three generations of 30 catalysts. With the help of automated sol−gel synthesis techniques, a high-throughput continuous flow reactor (16UPCFR), and appropriate software for experimental design, a new catalyst composition with improved performance has been obtained. Finally, the best catalysts were scaled-up to gram quantities and tested in a continuous-flow reactor unit that was equipped with four parallel reactors (4UPCFR). The final catalyst showed a significantly higher selectivity toward methacrolein at the same isobutane conversion, compared to the initial $Mo_8V_2Sb_{90}O_x$ catalyst.

Introduction

The optimization of heterogeneous catalysts by combinatorial principles is faced with the high complexity of the optimization task of comparing a large number of variables. This includes qualitative and quantitative aspects of catalyst composition, as well as the diversity of preparation parameters (such as type of precursors, calcination temperature, and calcination media) and operating conditions (such as temperature, contact time, and reactant concentrations). Therefore, effective experimental strategies are required to navigate through this vast experimental space in the search for new materials. A variety of methods have already been applied to the design of combinatorial experiments in heterogeneous catalysis, including statistical design of experiments,[1,2] diversity methods,[3] evolutionary algorithms,[4−6] neural networks,[7−9] and hybrid approaches.[10−12] The choice of strategy is dependent on the goals of the experiment and the intended use of the resulting data. An indication that evolutionary principles can be applied in heterogeneous catalysis has already been reported in the optimization of multicomponent oxides for the oxidative dehydrogenation of propane.[4] A significant increase in the propene yield was observed with the increasing number of generations.

In the present study, the best-performing $Mo_8V_2Sb_{90}O_x$ catalyst presented earlier for the selective oxidation of isobutane[13] is further optimized using an evolutionary approach that is based on a genetic algorithm. In particular, some dopants (M^1, M^2, and M^3), which were selected from elements such as Sb, Cr, Fe, Nb, Te, Ce, P and K, were added to the $Mo_8V_2Sb_{80}M^1_{10-k}M^2_{10-l}M^3_{10-m}O_x$ system ($k,l,m \in [0,10]$), based on their interesting dehydrogenation and/or oxidation properties of the associated oxides reported in the literature.[14] In this way, the purpose of these efforts was to increase the selectivity to methacrolein (MA) at the same (or even increased) isobutane conversion.

Results and Discussion

Optimization via Combinatorial Approaches. For combinatorial optimization with the genetic algorithm, the digitalization of material information was indispensable. Therefore, the composition of each additive was coded with a system of 8 digits. The size of each generation of catalysts and the initial number of elements per catalyst were 30 and 3, respectively. Table 1 shows how the first generation has been produced by two random number sets. For the selection of three elements, a binary system with 8 digits was used. Thirty 8-digit numbers, which consisted of five “zeros” and three “ones”, were selected in a random way for the determination of the elements included in the catalytic materials of the first generation. The digit “0” represents the absence of an element, and the digit “1” denotes its presence in the catalyst. In this way, each catalytic material consisted of three primary components. For the determination of the elemental composition of each element, 90 (30 × 3) numbers consisting of a real number between 0 and 100 were created randomly. These numbers were then normalized so that the sum of the three dopants was equal to 10. Each number corresponded to the relative amount of three elements determined by the 8 digits, given in order. In this way, the digits in the code for elemental composition referred to the molar concentration of the corresponding elements in the catalyst.

In a first round, these catalytic materials were then screened for their dehydrogenation, oxygenation, and total oxidation properties in the high-throughput continuous-flow

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Table 1. Production of the First Generation of Doped $MoVSbO_x$ Catalysts by Two Random Number Sets[a]

existence	quantity	catalyst number	Molar Concentration (%)								composition
			Sb	Cr	Fe	Nb	Te	Ce	P	K	
[1 0 0 0 0 1 0 1]	[1.9 0.1 8.0]	1	1.9					0.1		8.0	$Mo_8V_2Sb_{81.9}Cr_0Fe_0Nb_0Te_0Ce_{0.1}P_0K_{8.0}O_x$
[1 0 1 0 0 0 0 1]	[4.5 3.3 2.2]	2	4.5		3.3					2.2	$Mo_8V_2Sb_{84.5}Cr_0Fe_{3.3}Nb_0Te_0Ce_0P_0K_{2.2}O_x$
[1 0 0 1 0 0 1 0]	[3.9 2.3 3.8]	3	3.9			2.3			3.8		$Mo_8V_2Sb_{83.9}Cr_0Fe_0Nb_{2.3}Te_0Ce_0P_{3.8}K_0O_x$
[0 0 1 1 0 0 0 1]	[3.7 3.4 2.9]	4			3.7	3.4				2.9	$Mo_8V_2Sb_{80.0}Cr_0Fe_{3.7}Nb_{3.4}Te_0Ce_0P_0K_{2.9}O_x$
[1 0 0 1 0 0 0 1]	[3.0 3.8 3.2]	5	3.0			3.8				3.2	$Mo_8V_2Sb_{83.0}Cr_0Fe_0Nb_{3.8}Te_0Ce_0P_0K_{3.2}O_x$
[0 1 0 1 0 1 0 0]	[2.0 3.3 4.7]	6		2.0		3.3		4.7			$Mo_8V_2Sb_{80.0}Cr_{2.0}Fe_0Nb_{3.3}Te_0Ce_{4.7}P_0K_0O_x$
[1 1 0 0 0 0 1 0]	[4.8 1.7 3.5]	7	4.8	1.7					3.5		$Mo_8V_2Sb_{84.8}Cr_{1.7}Fe_0Nb_0Te_0Ce_0P_{3.5}K_0O_x$
[0 0 1 0 0 1 1 0]	[3.4 3.4 3.2]	8			3.4			3.4	3.2		$Mo_8V_2Sb_{80.0}Cr_0Fe_{3.4}Nb_0Te_0Ce_{3.4}P_{3.2}K_0O_x$
[0 1 0 1 0 0 0 1]	[0.8 3.9 5.3]	9		0.8		3.9				5.3	$Mo_8V_2Sb_{80.0}Cr_{0.8}Fe_0Nb_{3.9}Te_0Ce_0P_0K_{5.3}O_x$
[1 0 1 1 0 0 0 0]	[3.0 2.0 5.0]	10	3.0		2.0	5.0					$Mo_8V_2Sb_{83.0}Cr_0Fe_{2.0}Nb_{5.0}Te_0Ce_0P_0K_0O_x$
[0 1 1 0 0 0 1 0]	[4.2 4.4 1.5]	11		4.2	4.4				1.5		$Mo_8V_2Sb_{80.0}Cr_{4.2}Fe_{4.4}Nb_0Te_0Ce_0P_{1.5}K_0O_x$
[0 0 0 0 1 1 0 1]	[1.5 3.6 4.9]	12					1.5	3.6		4.9	$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_0Te_{1.5}Ce_{3.6}P_0K_{4.9}O_x$
[0 1 0 1 0 0 0 1]	[1.7 1.5 6.8]	13		1.7		1.5				6.8	$Mo_8V_2Sb_{80.0}Cr_{1.7}Fe_0Nb_{1.5}Te_0Ce_0P_0K_{6.8}O_x$
[1 0 0 0 0 0 1 1]	[5.1 1.7 3.2]	14	5.1						1.7	3.2	$Mo_8V_2Sb_{85.1}Cr_0Fe_0Nb_0Te_0Ce_0P_{1.7}K_{3.2}O_x$
[1 1 0 0 0 0 1 0]	[2.8 5.0 2.2]	15	2.8	5.0					2.2		$Mo_8V_2Sb_{82.8}Cr_{5.0}Fe_0Nb_0Te_0Ce_0P_{2.2}K_0O_x$
[0 0 0 0 1 1 1 0]	[3.4 5.5 1.1]	16					3.4	5.5	1.1		$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_0Te_{3.4}Ce_{5.5}P_{1.1}K_0O_x$
[0 1 1 0 0 0 1 0]	[5.7 2.0 2.3]	17		5.7	2.0				2.3		$Mo_8V_2Sb_{80.0}Cr_{5.7}Fe_{2.0}Nb_0Te_0Ce_0P_{2.3}K_0O_x$
[0 1 0 0 1 1 0 0]	[1.0 5.6 3.4]	18		1.0			5.6	3.4			$Mo_8V_2Sb_{80.0}Cr_{1.0}Fe_0Nb_0Te_{5.6}Ce_{3.4}P_0K_0O_x$
[1 0 0 1 1 0 0 0]	[1.2 2.3 6.5]	19	1.2			2.3	6.5				$Mo_8V_2Sb_{81.2}Cr_0Fe_0Nb_{2.3}Te_{6.5}Ce_0P_0K_0O_x$
[1 0 1 1 0 0 0 0]	[3.0 2.0 5.0]	20	3.0		2.0	5.0					$Mo_8V_2Sb_{83.0}Cr_0Fe_{2.0}Nb_{5.0}Te_0Ce_0P_0K_0O_x$
[0 0 0 1 0 1 1 0]	[0.8 1.6 7.7]	21				0.8		1.6	7.7		$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_{0.8}Te_0Ce_{1.6}P_{7.7}K_0O_x$
[1 0 0 0 0 1 1 0]	[1.2 8.4 0.4]	22	1.2					8.4	0.4		$Mo_8V_2Sb_{81.2}Cr_0Fe_0Nb_0Te_0Ce_{8.4}P_{0.4}K_0O_x$
[1 0 0 1 0 0 0 1]	[4.5 1.6 4.0]	23	4.5			1.6				4.0	$Mo_8V_2Sb_{84.5}Cr_0Fe_0Nb_{1.6}Te_0Ce_0P_0K_{4.0}O_x$
[0 0 0 1 0 0 1 1]	[2.6 7.3 0.1]	24				2.6			7.3	0.1	$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_{2.6}Te_0Ce_0P_{7.3}K_{0.1}O_x$
[1 1 0 1 0 0 0 0]	[3.9 2.6 3.5]	25	3.9	2.6		3.5					$Mo_8V_2Sb_{83.9}Cr_{2.6}Fe_0Nb_{3.5}Te_0Ce_0P_0K_0O_x$
[0 0 0 1 1 1 0 0]	[0.5 3.9 5.7]	26				0.5	3.9	5.7			$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_{0.5}Te_{3.9}Ce_{5.7}P_0K_0O_x$
[1 0 0 1 0 0 1 0]	[1.7 4.1 4.3]	27	1.7			4.1			4.3		$Mo_8V_2Sb_{81.7}Cr_0Fe_0Nb_{4.1}Te_0Ce_0P_{4.3}K_0O_x$
[0 0 1 0 0 0 1 1]	[3.0 1.7 5.3]	28			3.0				1.7	5.3	$Mo_8V_2Sb_{80.0}Cr_0Fe_{3.0}Nb_0Te_0Ce_0P_{1.7}K_{5.3}O_x$
[0 0 0 0 0 1 1 1]	[0.4 2.8 6.8]	29						0.4	2.8	6.8	$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_0Te_0Ce_{0.4}P_{2.8}K_{6.8}O_x$
[1 1 0 0 0 0 0 1]	[0.6 6.6 2.9]	30	0.6	6.6						2.9	$Mo_8V_2Sb_{80.6}Cr_{6.6}Fe_0Nb_0Te_0Ce_0P_0K_{2.9}O_x$

[a] Existence × quantity = composition.

reactor (16UPCFR). One reactor tube was filled with quartz grains, to check the contribution of a homogeneous reaction. The main products formed included carbon monoxide (CO), carbon dioxide (CO_2), isobutene, and methacrolein (MA). The formation of C_1, C_2, and/or C_3 molecules, as well as other oxygenates, could not be observed in the present set of experiments. (The corresponding results are listed later in this work in Table 3, in order of decreasing methacrolein selectivity (S_{MA}) at 1% isobutane (i-C_4) conversion.) It was noticed that doping the $Mo_8V_2Sb_{90}O_x$ mixed oxide with small amounts of niobium and tellerium developed the highest selectivity toward MA; i.e., $S_{MA} = 50.4\%$ for the $Mo_8V_2Sb_{81.2}Nb_{2.3}Te_{6.5}O_x$ composition. On the other hand, other metal oxide compositions also showed selectivities of $S_{MA} = 43.7\%$ and 26.5% for $Mo_8V_2Sb_{80}Te_{3.4}Ce_{5.5}P_{1.1}O_x$ and $Mo_8V_2Sb_{83}Fe_2Nb_5O_x$, respectively. Finally, those catalysts with a catalytic activity of <1% in the temperature range tested had CO_x, isobutene, and MA selectivities that were equal to zero.

After analysis of the performance of the first-generation catalysts for the selective oxidation of isobutane, a second generation of catalysts was planned. For the selection of catalytic materials in an ongoing evolutionary procedure, different criteria (e.g., i-C_4 conversion, MA yield or selectivity) could have been used to identify the promising materials. Because methacrolein is the desired product, which is formed as an intermediate in a sequence of oxidation steps, MA selectivity at 1% i-C_4 conversion was used throughout the entire evolutionary procedure for the evaluation of subsequent generations of catalysts.

Table 2 illustrates the reproduction procedure for the second generation of catalysts, based on the evaluation results of the first generation of catalysts, using the normalized performance of each catalyst, based on the MA selectivity ("Norm No."), the type of operation ("Operator"), the corresponding parent(s) ("Parent"), and the place where the operation starts ("C/M position"). Based on the selectivities toward MA, the "runlet selection" was performed to choose between the three evolutionary operators, i.e., crossover, quantitative, and qualitative mutation.[4] In addition, the same population size was used in all subsequent generations. Finally, after performing one of the three operations, the antimony content for each generated catalyst was adapted to keep the total concentration of elements equal to 100%.

In particular, for the reproduction of the second generation of catalysts, 10 catalysts were generated by quantitative mutation. For example, the first catalyst of the second generation was created by taking catalyst 10 of the first generation (based on the fitness proportional choice) and altering the element concentration on position 4 (niobium) from 5% to 7.5%. In addition, two catalysts were generated by qualitative mutation. For instance, in the second generation, catalyst 20 was generated by changing the molar concentration of iron (from 0% to 2.1%) in catalyst 16 of the first generation. Finally, 18 catalysts were created by crossover. Catalysts 5 and 6 from the second generation, for instance, were generated by crossover at position 2 between the fitness proportional selected catalyst 30 and the randomly chosen catalyst 19 (both from the first generation).

Table 2. Reproduction Procedure of the Second Generation with Operations of Crossover and Mutation

1st generation results			Operation (crossover + mutation)										
Cat No.	Selectivity MA (%)	Norm No. [a]	Parent	Dopant								Operator [b]	C/M Pos [c]
				Sb	Cr	Fe	Nb	Te	Ce	P	K		
1	8.4	1	10	3.0		2.0	5.0					Quant	4
2	7.2	1	24				2.6			7.3	0.09	Quant	4
3	5.1	0	21				0.8		1.6	7.7		Quant	6
4	7.8	1	19	1.2			2.3	6.5				Quant	5
5	7.7	1	30	0.6	6.6						2.9	Cross	2
6	13.2	1	19	1.2			2.3	6.5					
7	8.3	1	23	4.5			1.6				3.9	Cross	1
8	15.8	1	10	3.0		2.0	5.0						
9	7.5	1	27	1.7			4.1			4.3		Cross	3
10	26.5	2	30	0.6	6.6						2.9		
11	6.9	1	19	1.2			2.3	6.5				Cross	3
12	11.4	1	16					3.4	5.5	1.1			
13	8.0	1	14	5.1						1.7	3.2	Quant	8
14	8.6	1	18		1.0			5.6	3.4			Cross	4
15	4.8	0	19	1.2			2.3	6.5					
16	43.7	4	16					3.4	5.5	1.1		Quant	5
17	4.3	0	16					3.4	5.5	1.1		Cross	5
18	12.6	1	10	3.0		2.0	5.0						
19	50.4	4	15	2.8	5.0					2.2		Quant	2
20	21.7	2	16					3.4	5.5	1.1		Qual	3
21	10.3	1	19	1.2			2.3	6.5				Quant	4
22	0	0	11		4.2	4.4				1.5		Qual	5
23	7.1	1	5	3.0			3.8				3.2	Cross	5
24	10.9	1	19	1.2			2.3	6.5					
25	21.8	2	20	3.0		2.0	5.0					Quant	3
26	0	0	12					1.5	3.6		4.9	Cross	3
27	20.4	2	23	4.5			1.5				4.0		
28	0	0	12					1.5	3.6		4.9	Cross	4
29	8.6	1	3	3.9			2.3			3.8			
30	9.8	1	19	1.2			2.3	6.5				Quant	4

2nd generation

Cat No.	Dopant								Catalyst Composition
	Sb	Cr	Fe	Nb	Te	Ce	P	K	
1	0.5		2.0	7.5					$Mo_8V_2Sb_{80.5}Cr_0Fe_2Nb_{7.5}Te_0Ce_0P_0K_0$
2	-1.3			3.9			7.3	0.09	$Mo_8V_2Sb_{78.7}Cr_0Fe_0Nb_{3.9}Te_0Ce_0P_{7.3}K_{0.09}$
3	-0.8			0.8		2.3	7.7		$Mo_8V_2Sb_{79.2}Cr_0Fe_0Nb_{0.8}Te_0Ce_{2.3}P_{7.7}K_0$
4	-2.0			2.3	9.7				$Mo_8V_2Sb_{78.0}Cr_0Fe_0Nb_{2.3}Te_{9.7}Ce_0P_0K_0$
5	-5.4	6.6		2.3	6.5				$Mo_8V_2Sb_{74.6}Cr_{6.6}Fe_0Nb_{2.3}Te_{6.5}Ce_0P_0K_0$
6	7.1							2.9	$Mo_8V_2Sb_{87.1}Cr_0Fe_0Nb_0Te_0Ce_0P_0K_{2.9}$
7	3.0		2.0	5.0					$Mo_8V_2Sb_{83.0}Cr_0Fe_2Nb_5Te_0Ce_0P_0K_0$
8	4.5			1.6				3.9	$Mo_8V_2Sb_{84.5}Cr_0Fe_0Nb_{1.6}Te_0Ce_0P_0K_{3.9}$
9	7.1							2.9	$Mo_8V_2Sb_{87.1}Cr_0Fe_0Nb_0Te_0Ce_0P_0K_{2.9}$
10	-5.0	6.6		4.1			4.3		$Mo_8V_2Sb_{75.0}Cr_{6.6}Fe_0Nb_{4.1}Te_0Ce_0P_{4.3}K_0$
11					3.4	5.5	1.1		$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_0Te_{3.4}Ce_{5.5}P_{1.1}K_0$
12	1.2			2.3	6.5				$Mo_8V_2Sb_{81.2}Cr_0Fe_0Nb_{2.3}Te_{6.5}Ce_0P_0K_0$
13	6.7						1.7	1.6	$Mo_8V_2Sb_{86.7}Cr_0Fe_0Nb_0Te_0Ce_0P_{1.7}K_{1.6}$
14	2.5	1.0			6.5				$Mo_8V_2Sb_{82.5}Cr_{1.0}Fe_0Nb_0Te_{6.5}Ce_0P_0K_0$
15	-1.3			2.3	5.6	3.4			$Mo_8V_2Sb_{78.7}Cr_0Fe_0Nb_{2.3}Te_{5.6}Ce_{3.4}P_0K_0$
16	-1.7				5.1	5.5	1.1		$Mo_8V_2Sb_{78.3}Cr_0Fe_0Nb_0Te_{5.1}Ce_{5.5}P_{1.1}K_0$
17	6.6				3.4				$Mo_8V_2Sb_{86.6}Cr_0Fe_0Nb_0Te_{3.4}Ce_0P_0K_0$
18	-3.6		2.0	5.0		5.5	1.1		$Mo_8V_2Sb_{76.4}Cr_0Fe_{2.0}Nb_{5.0}Te_0Ce_{5.5}P_{1.1}K_0$
19	5.3	2.5					2.2		$Mo_8V_2Sb_{85.3}Cr_{2.5}Fe_0Nb_0Te_0Ce_0P_{2.2}K_0$
20	2.1		2.1		3.4	5.5	1.1		$Mo_8V_2Sb_{77.9}Cr_0Fe_{2.1}Nb_0Te_{3.4}Ce_{5.5}P_{1.1}K_0$
21	2.3			1.2	6.5				$Mo_8V_2Sb_{82.3}Cr_0Fe_0Nb_{1.2}Te_{6.5}Ce_0P_0K_0$
22	-7.7	4.2	4.4		7.6		1.5		$Mo_8V_2Sb_{72.3}Cr_{4.2}Fe_{4.4}Nb_0Te_{7.6}Ce_0P_{1.5}K_0$
23	6.2			3.8					$Mo_8V_2Sb_{86.2}Cr_0Fe_0Nb_{3.8}Te_0Ce_0P_0K_0$
24	-2.0			2.3	6.5			3.2	$Mo_8V_2Sb_{78.0}Cr_0Fe_0Nb_{2.3}Te_{6.5}Ce_0P_0K_{3.2}$
25	2.0		3.0	5.0					$Mo_8V_2Sb_{82.0}Cr_0Fe_3Nb_5Te_0Ce_0P_0K_0$
26	4.5				1.5			4.0	$Mo_8V_2Sb_{84.5}Cr_0Fe_0Nb_{1.5}Te_0Ce_0P_0K_{4.0}$
27	0				1.5	3.6		4.9	$Mo_8V_2Sb_{80.0}Cr_0Fe_0Nb_0Te_{1.5}Ce_{3.6}P_0K_{4.9}$
28	6.2						3.8		$Mo_8V_2Sb_{86.2}Cr_0Fe_0Nb_0Te_0Ce_0P_{3.8}K_0$
29	-2.3			2.3	1.5	3.6		4.9	$Mo_8V_2Sb_{77.7}Cr_0Fe_0Nb_{2.3}Te_{1.5}Ce_{3.6}P_0K_{4.9}$
30	0.1			3.4	6.5				$Mo_8V_2Sb_{80.1}Cr_0Fe_0Nb_{3.4}Te_{6.5}Ce_0P_0K_0$

[a] Normalized frequency of catalyst presence in next generation. [b] Cross = crossover; quant = quantitative mutation; qual = qualitative mutation. [c] Crossover/mutation position.

The number of created generations may be increased continuously according to the procedure described above. In the present study, three generations were prepared and screened in this manner. In this way, the total number of tested catalysts amounted to 90. The results for the corresponding catalysts in the successive generations are ranked in Table 3.

Clearly, the selectivity toward MA for the 10 best catalysts has increased significantly from the first generation to the third generation: the best catalyst in generations 1, 2, and 3 showed S_{MA} values of 50.4%, 53.5%, and 55.8%, respectively, compared to 35.8% for the initial $Mo_8V_2Sb_{90}O_x$ catalyst (Figure 1). The figure shows that not only the MA selectivity, but also the number of selective catalysts grows during the evolutionary changes. After identification of the amount of “doping” elements present in the 10 best catalysts, it was interesting to note that, primarily, the presence of niobium and tellurium seems to be essential (Figure 2). However, even the best materials still contained minor amounts of chromium, iron, cerium, phosphorus, and potassium. Therefore, it could not be decided yet whether the presence of minor amounts of these elements is of any significance.

Scaling Up the Best Catalyst Compositions. After the significant increase in MA selectivity with three catalyst generations, the decision was made to stop the evolutionary design strategy and examine the hits using conventional techniques. The seven best materials from the combinatorial screening stage with the highest MA selectivity were prepared and tested by conventional experiments (in a continuous-flow reactor unit with four parallel reactors (4UPCFR)), using 500 mg of pelletized catalyst per reactor.

Table 4 shows the composition, the oxygen conversion, and the selectivities toward the different products at 1% isobutane conversion for different oxide catalysts tested in the 4UPCFR. These data were derived from a data set that contained conversion data and selectivities at different temperatures. In all cases, the isobutane conversion showed an exponentional change with a change of reaction temperature. Using regression analysis, the selectivity for the different products at 1% isobutane conversion could be determined. The obtained selectivities were comparable to those obtained in the 16UPCFR. It is important to note that the order of catalyst performance (in terms of MA selectivity) determined in the high-throughput screening from the first generation of catalysts to the third generation of catalysts remained identical in the scaling-up tests. Particularly, the selectivity to MA, for the best catalyst compositions in each generation, increased from 40.2% for the initial catalyst composition ($Mo_8V_2Sb_{90}O_x$) to 46.9% (first generation), 52.6% (second generation), and 52.8% (third generation).

To determine the influence of isobutane conversion on the MA, isobutene, and CO_x selectivities, the contact time was varied by changing the flow rate at 400 °C over the best performing catalyst composition from each generation. A gradual increase of MA selectivities was observed from the initial $Mo_8V_2Sb_{90}O_x$ catalyst composition to the best performing catalyst compositions of every further generation in the evolutionary process, in the isobutane conversion range studied (Figure 3). For instance, the selectivity toward MA at 3% isobutane conversion increased from 25.8% for the $Mo_8V_2Sb_{90}O_x$ catalyst to 44.7% for the best-performing catalyst from the third generation. At the same time, a decrease in isobutene and CO_x selectivities was observed for the best catalyst of the consecutive generations. These results were in good agreement with the results obtained from the high-throughput screening in the 16-fold reactor.

Table 3. Compositions for the First, Second, and Third Generation and Their Selectivity toward Methacrolein (S_{MA}) at 1% Isobutane Conversion

composition	S_{MA} (%)	composition	S_{MA} (%)
First Generation			
$Mo_8V_2Sb_{81.2}Nb_{2.3}Te_{6.5}O_x$	50.4	$Mo_8V_2Sb_{81.9}Ce_{0.1}K_{8.0}O_x$	8.4
$Mo_8V_2Sb_{80}Te_{3.4}Ce_{5.5}P_{1.1}O_x$	43.7	$Mo_8V_2Sb_{84.8}Cr_{1.7}P_{3.5}O_x$	8.3
$Mo_8V_2Sb_{83}Fe_2Nb_5O_x$	26.5	$Mo_8V_2Sb_{80}Cr_{1.7}Nb_{1.5}K_{6.8}O_x$	8.0
$Mo_8V_2Sb_{83.9}Cr_{2.6}Nb_{3.5}O_x$	21.8	$Mo_8V_2Sb_{80}Fe_{3.7}Nb_{3.4}K_{2.9}O_x$	7.8
$Mo_8V_2Sb_{83.0}Fe_{2.0}Nb_{5.0}O_x$	21.7	$Mo_8V_2Sb_{83.0}Nb_{3.8}K_{3.2}O_x$	7.7
$Mo_8V_2Sb_{81.7}Nb_{4.1}P_{4.3}O_x$	20.4	$Mo_8V_2Sb_{80}Cr_{0.8}Nb_{3.9}K_{5.3}O_x$	7.5
$Mo_8V_2Sb_{80}Fe_{3.4}Ce_{3.4}P_{3.2}O_x$	15.8	$Mo_8V_2Sb_{84.5}Fe_{3.3}K_{2.2}O_x$	7.2
$Mo_8V_2Sb_{80}Cr_{2.0}Nb_{3.3}Ce_{4.7}O_x$	13.2	$Mo_8V_2Sb_{84.5}Nb_{1.6}K_{4.0}O_x$	7.0
$Mo_8V_2Sb_{80}Cr_{1.0}Te_{5.6}Ce_{3.4}O_x$	12.6	$Mo_8V_2Sb_{80}Cr_{4.2}Fe_{4.4}P_{1.5}O_x$	6.9
$Mo_8V_2Sb_{80}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	11.4	$Mo_8V_2Sb_{83.9}Nb_{2.3}P_{3.8}O_x$	5.1
$Mo_8V_2Sb_{80}Nb_{2.6}P_{7.3}K_{0.1}O_x$	10.9	$Mo_8V_2Sb_{82.8}Cr_5P_{2.2}O_x$	4.8
$Mo_8V_2Sb_{80}Nb_{0.8}Ce_{1.6}P_{7.7}O_x$	10.3	$Mo_8V_2Sb_{80}Cr_{5.7}Fe_{2.0}P_{2.3}O_x$	4.2
$Mo_8V_2Sb_{80.6}Cr_{6.6}K_{2.9}O_x$	9.8	$Mo_8V_2Sb_{81.2}Ce_{8.4}P_{0.4}O_x$	0^a
$Mo_8V_2Sb_{80}Ce_{0.4}P_{2.8}K_{6.8}O_x$	8.6	$Mo_8V_2Sb_{80}Nb_{0.5}Te_{3.9}Ce_{5.7}O_x$	0^a
$Mo_8V_2Sb_{85.1}P_{1.7}K_{3.2}O_x$	8.6	$Mo_8V_2Sb_{80}Fe_{3.0}P_{1.7}K_{5.3}O_x$	0^a
		average	**12.3**
Second Generation			
$Mo_8V_2Sb_{78.0}Nb_{2.3}Te_{9.7}O_x$	53.5	$Mo_8V_2Sb_{78.3}Te_{5.1}Ce_{5.5}P_{1.1}O_x$	23.5
$Mo_8V_2Sb_{82.3}Nb_{1.2}Te_{6.5}O_x$	52.7	$Mo_8V_2Sb_{82.5}Cr_{1.0}Te_{6.5}O_x$	22.5
$Mo_8V_2Sb_{86.2}Nb_{3.8}O_x$	51.1	$Mo_8V_2Sb_{86.6}Te_{3.4}O_x$	20.3
$Mo_8V_2Sb_{81.2}Nb_{2.3}Te_{6.5}O_x$	50.8	$Mo_8V_2Sb_{72.3}Cr_{4.2}Fe_{4.4}Te_{7.6}P_{1.5}O_x$	18.4
$Mo_8V_2Sb_{77.9}Fe_{2.1}Te_{3.4}Ce_{5.5}P_{1.1}O_x$	50.0	$Mo_8V_2Sb_{85.3}Cr_{2.5}P_{2.2}O_x$	15.0
$Mo_8V_2Sb_{78.7}Nb_{2.3}Te_{5.6}Ce_{3.4}O_x$	49.6	$Mo_8V_2Sb_{80.1}Nb_{3.4}Te_{6.5}O_x$	14.8
$Mo_8V_2Sb_{77.7}Nb_{2.3}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	46.5	$Mo_8V_2Sb_{82.0}Fe_{3.0}Nb_{5.0}O_x$	14.7
$Mo_8V_2Sb_{78.0}Nb_{2.3}Te_{6.5}K_{3.2}O_x$	36.6	$Mo_8V_2Sb_{79.2}Nb_{0.8}Ce_{2.3}P_{7.7}O_x$	14.1
$Mo_8V_2Sb_{87.1}K_{2.9}O_x$	35.4	$Mo_8V_2Sb_{86.2}P_{3.8}O_x$	12.4
$Mo_8V_2Sb_{74.6}Cr_{6.6}Nb_{2.3}Te_{6.5}O_x$	31.7	$Mo_8V_2Sb_{84.5}Nb_{1.5}K_{4.0}O_x$	8.7
$Mo_8V_2Sb_{80.0}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	29.4	$Mo_8V_2Sb_{75.0}Cr_{6.6}Nb_{4.1}P_{4.3}O_x$	8.2
$Mo_8V_2Sb_{86.7}P_{1.7}K_{1.6}O_x$	28.8	$Mo_8V_2Sb_{84.5}Nb_{1.5}K_{4.0}O_x$	6.5
$Mo_8V_2Sb_{80.5}Fe_{2.0}Nb_{7.5}O_x$	28.6	$Mo_8V_2Sb_{76.4}Fe_{2.0}Nb_{5.0}Ce_{5.5}P_{1.1}O_x$	4.0
$Mo_8V_2Sb_{83.0}Fe_{2.0}Nb_{5.0}O_x$	24.2	$Mo_8V_2Sb_{81.1}Ce_{4.0}K_{4.9}O_x$	0^a
$Mo_8V_2Sb_{78.7}Nb_{3.9}P_{7.3}K_{0.09}O_x$	23.7	$Mo_8V_2Sb_{80.0}Te_{3.4}Ce_{5.5}P_{1.1}O_x$	0^a
		average	**25.9**
Third Generation			
$Mo_8V_2Sb_{79.3}Cr_{0.2}Fe_{2.1}Nb_{0.7}Te_{1.1}Ce_{5.5}P_{1.1}O_x$	55.8	$Mo_8V_2Sb_{79.7}Cr_{0.5}Te_{5.6}Ce_{3.4}K_{0.8}O_x$	26.7
$Mo_8V_2Sb_{83.5}Nb_{2.3}P_{4.3}O_x$	55.1	$Mo_8V_2Sb_{81.1}Nb_{5.7}K_{3.2}O_x$	24.9
$Mo_8V_2Sb_{76.6}Nb_{3.4}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	53.3	$Mo_8V_2Sb_{67.1}Cr_{9.3}Fe_{5.3}Nb_{0.9}P_{7.3}K_{0.1}O_x$	23.5
$Mo_8V_2Sb_{80.3}Te_{5.1}Ce_{3.3}P_{1.3}K_{0.003}O_x$	53.0	$Mo_8V_2Sb_{78.4}Fe_{5.3}Nb_{2.3}Te_{6.5}K_{2.9}O_x$	21.7
$Mo_8V_2Sb_{82.8}Nb_{2.3}Te_{4.9}O_x$	51.2	$Mo_8V_2Sb_{77.5}Cr_{2.5}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	16.1
$Mo_8V_2Sb_{73.1}Nb_{2.3}Te_{14.6}O_x$	48.8	$Mo_8V_2Sb_{84.5}Nb_{2.3}Te_{3.2}O_x$	15.5
$Mo_8V_2Sb_{80.1}Nb_{3.4}Te_{6.5}O_x$	48.4	$Mo_8V_2Sb_{83.4}Cr_{6.6}O_x$	14.8
$Mo_8V_2Sb_{78.9}Cr_{0.2}Fe_{2.1}Nb_{2.3}Te_{6.5}O_x$	45.3	$Mo_8V_2Sb_{78.0}Cr_{1.0}Te_{5.6}Ce_{3.4}K_2O_x$	12.8
$Mo_8V_2Sb_{88.6}K_{1.4}O_x$	39.1	$Mo_8V_2Sb_{85.5}Nb_{2.3}P_{2.2}O_x$	12.0
$Mo_8V_2Sb_{81.6}Nb_{1.6}P_{2.9}K_{4.0}O_x$	38.6	$Mo_8V_2Sb_{83.4}Cr_{6.6}K_{2.9}O_x$	11.6
$Mo_8V_2Sb_{90}O_x$	35.8	$Mo_8V_2Sb_{57.2}Cr_{9.3}Fe_{5.3}Nb_{0.9}Te_{3.8}Ce_{4.0}P_{4.6}K_{4.9}O_x$	8.6
$Mo_8V_2Sb_{78.4}Nb_{2.3}Te_{6.5}K_{2.8}O_x$	35.8	$Mo_8V_2Sb_{83.6}Nb_{0.7}Te_{1.1}Ce_{3.3}P_{1.3}K_{0.003}O_x$	0^a
$Mo_8V_2Sb_{72.8}Cr_{6.6}Nb_{4.1}Te_{6.5}O_x$	31.0	$Mo_8V_2Sb_{78.1}Cr_{6.6}K_{5.3}O_x$	0^a
$Mo_8V_2Sb_{87.5}P_{1.7}K_{0.8}O_x$	29.6	$Mo_8V_2Sb_{64.9}Nb_{3.9}Te_{7.6}Ce_{4.0}P_{4.6}K_{4.9}O_x$	0^a
$Mo_8V_2Sb_{80.5}Cr_{0.5}Te_{5.6}Ce_{3.4}O_x$	28.4	$Mo_8V_2Sb_{80.2}Nb_{2.3}Te_{1.5}Ce_{3.6}K_{2.4}O_x$	0^a
		average	**27.9**

Conclusions

In this work, the use of a combinatorial search strategy was proposed for the optimization of sol−gel-synthesized $Mo_8V_2Sb_{90}O_x$ catalysts by determining the effect of the introduction of seven selected dopants. This approach required the introduction and optimization of automated synthesis and screening of catalysts by high-throughput techniques, as well as advanced software. In addition, an appropriate experimental design strategy had to be developed, to guide the screening in a much faster way. Based on the evolutionary approach reported earlier,[4] three consecutive generations of 30 catalysts were synthesized and screened in high-throughput mode. The high-throughput screening results showed a gradual increase in methacrolein (MA) selectivity at constant isobutane conversion for the best catalysts from each consecutive generation. After scaling-up the best-performing catalyst compositions from each generation, the results from the high-throughput screening could be reproduced on a gram scale. In this way, this study has, once again, confirmed the strength of using a combinatorial approach in catalyst research.

Experimental Section

Combinatorial Platform. For the automated catalyst synthesis, a Genesis RSP100 (TECAN) liquid handler was used. Because solvents as well as alkoxide precursor solu-

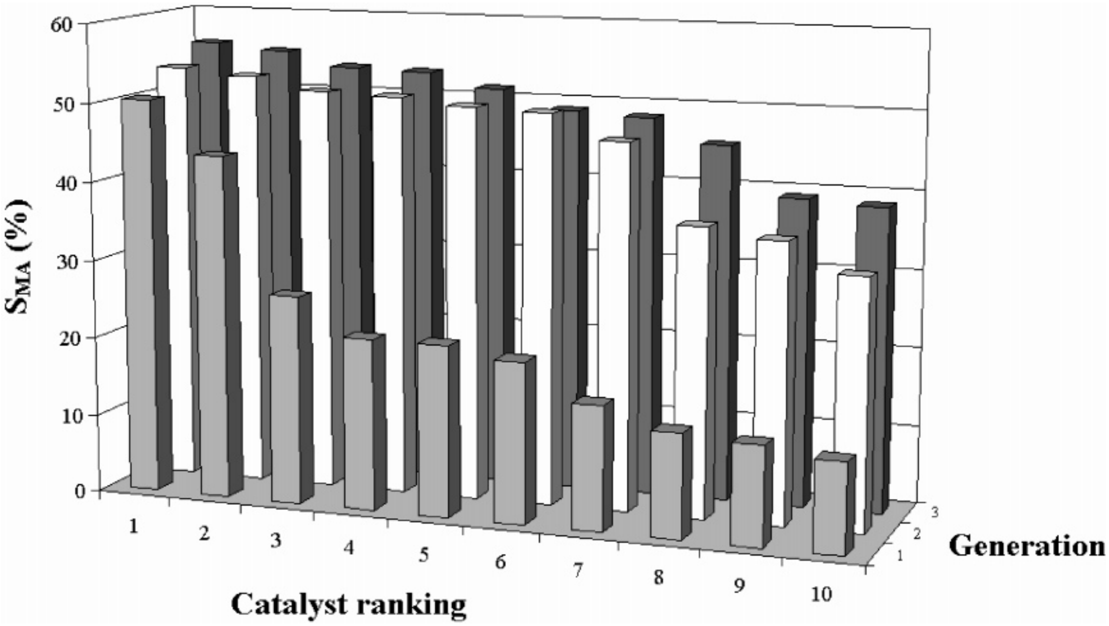

Figure 1. Change in methacrolein selectivity (S_{MA}) of the 10 best catalysts obtained with a genetic algorithm in three successive generations.

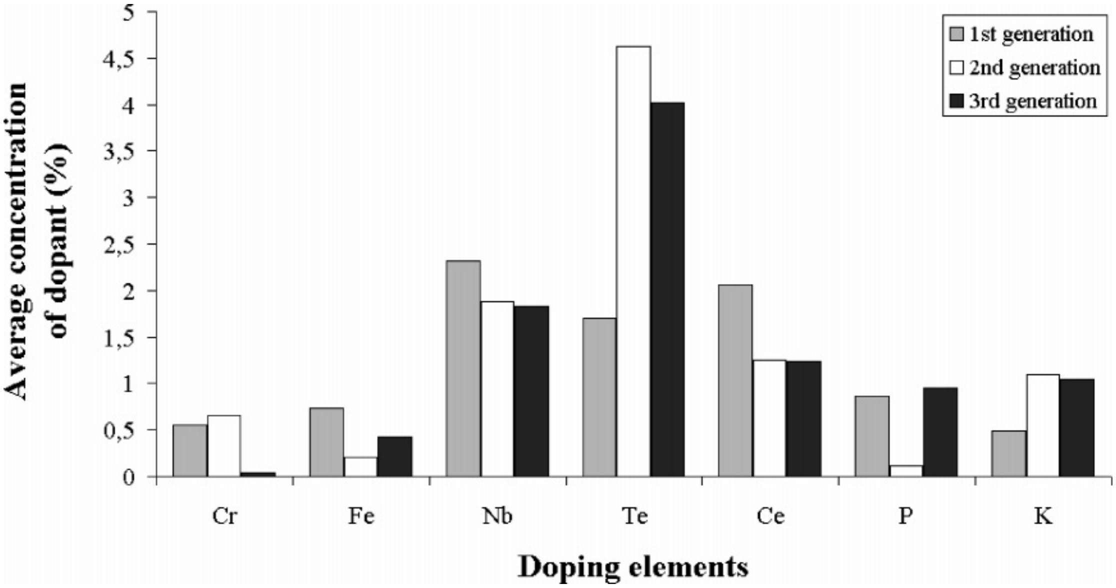

Figure 2. Effect of the evolutionary procedure on the average concentration of doping elements in the 10 best catalysts per generation.

Table 4. Overall Composition and Product Selectivities at 1% Isobutane Conversion for the Best Catalysts Tested in the 4UPCF Reactor[a]

			Selectivity (%)		
catalyst	generation	temperature, T (°C)	methacrolein, S_{MA}	isobutene, $S_{i-C_4^=}$	CO + CO$_2$, S_{CO_x}
$Mo_8V_2Sb_{90}O_x$	init[b]	391.7	40.2	30.9	26.8
$Mo_8V_2Sb_{81.2}Nb_{2.3}Te_{6.5}O_x$	1	403.1	46.9	27.6	23.5
$Mo_8V_2Sb_{78.0}Nb_{2.3}Te_{9.7}O_x$	2	464.4	52.6	23.4	22.4
$Mo_8V_2Sb_{77.7}Nb_{2.3}Te_{1.5}Ce_{3.6}K_{4.9}O_x$	2	447.0	44.7	27.6	24.1
$Mo_8V_2Sb_{79.3}Cr_{0.2}Fe_{2.1}Nb_{0.7}Te_{1.1}Ce_{5.5}P_{1.1}O_x$	3	462.3	52.8	23.0	20.6
$Mo_8V_2Sb_{83.5}Nb_{2.3}P_{4.3}O_x$	3	431.9	50.1	19.1	27.7
$Mo_8V_2Sb_{80.3}Te_{5.1}Ce_{3.3}P_{1.3}K_{0.003}O_x$	3	441.6	47.0	21.2	30.5
$Mo_8V_2Sb_{82.8}Nb_{2.3}Te_{4.9}O_x$	3	401.1	46.4	28.2	21.4

[a] Experimental conditions: total flow rate, 10 mL/min; i-C_4:O_2:He volume ratio, 3:1:2; mass of catalyst: 0.5 g. [b] Initial catalyst composition.

tions were used, a combination of two disposable tips (DITIs) and two fixed tips was chosen. Custom racks were built for the precursor solutions, as well as for the destination wells for catalyst synthesis. The destination rack could hold 30 22-mL wells. The synthesis of the combinatorial catalyst libraries was drastically accelerated by the use of an in-house

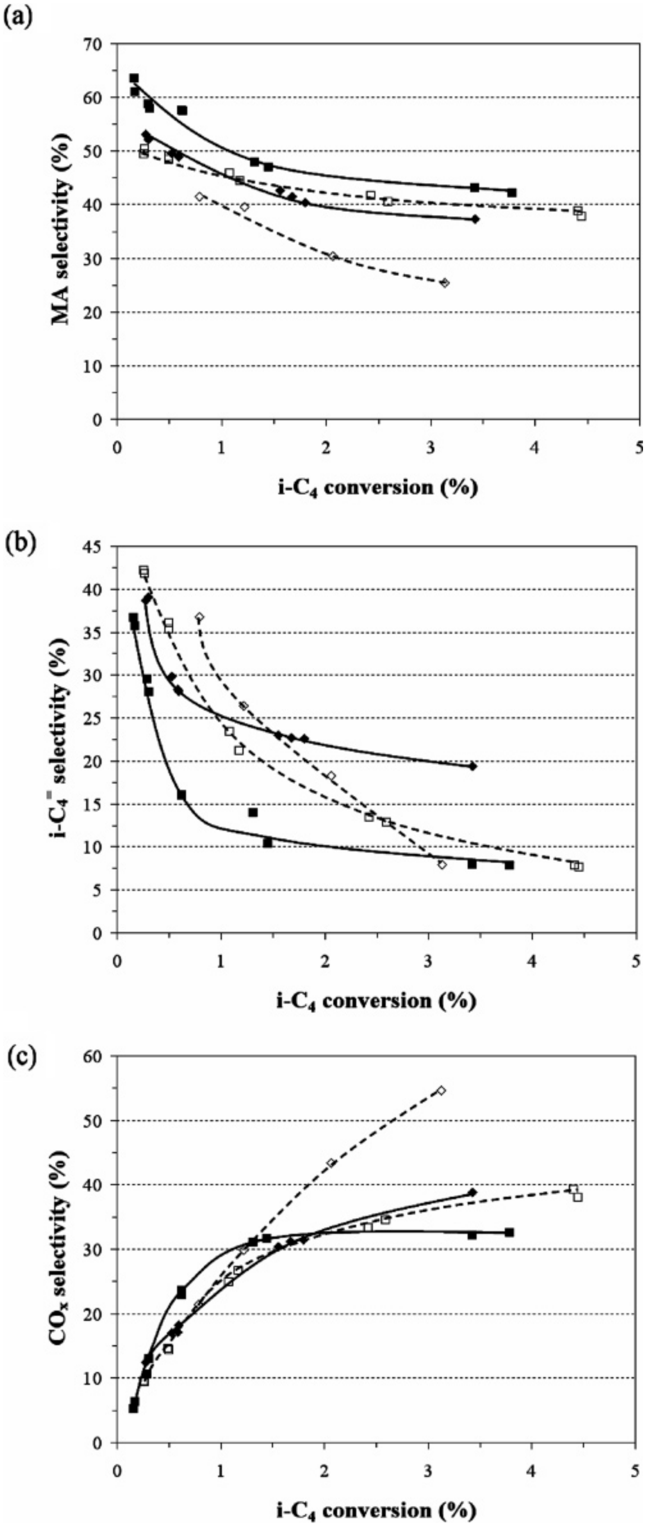

Figure 3. Product selectivities against isobutane conversion by changing the contact time at 400 °C for the best performing catalysts from each generation: (◇) initial catalyst, (◆) best first-generation catalyst, (□) best second-generation catalyst, and (■) best third-generation catalyst.

developed library design software, denoted as Pipetting Studio, written under MS Visual Basic.

For the synthesis, a modified acid-catalyzed sol−gel procedure (eq 1) was applied, based on the synthesis procedure for amorphous mixed oxides,[15] which lend themselves well to the use of dispensing robots:

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

0.5 M metal alkoxide precursor solutions were prepared by dissolving commercially available metal alkoxides (vanadium(V) triisopropoxide, molybdenum(V) isopropoxide 5% w/v in 2-propanol, chromium(III) isopropoxide 10−12% in 2-propanol, iron(III) ethoxide, niobium(V) ethoxide, tellurium(IV) ethoxide 85% v/v) or inorganic salts (ammonium cerium hexanitrate, phosphoric acid (85% v/v), potassium hydroxide, and anhydrous antimony(V) chloride) in 2-propanol. In the case of antimony(V) chloride, the solution was flushed with argon to remove the HCl vapors that formed. Proton acidity originated from a 0.15 M acetic acid solution in 2-propanol.

The total amount of reagents used was 8 mmol per flask. After the addition of all the reagents to each flask in a rack, the wells in the destination rack were closed, after which the rack was placed on an orbital shaker (Heidolph Unimax 1010) for 1 h to obtain a homogeneous solution. The destination rack was then kept covered overnight, to allow gel formation, after which point the lids were removed and the rack was placed under the hood for 3 days to allow the catalysts to dry. The resulting gels were calcined at 250 °C for 5 h (at a heating rate of 0.5 °C/min) and at 400 °C for 8 h (at a heating rate of 0.5 °C/min). The obtained powders were milled in the flasks and pelletized manually to a 0.125−0.250 mm size fraction, and finally 100 mg of each catalyst were transferred to the corresponding reactor tube in the 16-unit parallel continuous-flow reactor (16UPCFR).[16]

The 16UPCFR contained 16 open, quartz microreactor tubes mounted with Teflon ferrules (Swagelok) on a stainless-steel flange. The reactor set was covered with a quartz bulb that was sealed to the flange with a Kalrez O-ring. The upper portion of the tubes had an internal diameter of 2.1 mm and a height of 25 mm, and the tubes contained a quartz frit at the bottom to support the individual catalyst beds. Downstream from these frits, the quartz tubes were narrowed to an inner diameter (ID) of 1 mm. The feed inlet occurs through the flange. The entire reactor is electrically heated via a ceramic mantle with a control thermocouple. The actual temperature in the reactor is monitored by a thermocouple in the center of the reactor at catalyst bed height. The space between the different reactor tubes is filled with quartz cylinders, to reduce the death volume and possibly homogeneous reactions. The microreactor outlets are connected downstream to identical capillaries that create a major flow resistance, compared to that of the catalyst bed, ensuring an equal feed distribution over the 16 catalyst beds.

During the catalyst testing procedure, a continuous flow of feed gases passed through each catalyst bed. A flow of 20% oxygen in helium was used for catalyst pretreatment at 400 °C for 2 h. An isobutane/oxygen/helium feed (7.5/2.5/150 mL/min) was then fed over the different catalyst beds, corresponding to a space time (W/F_0) of 2.5 mg s/mL per reactor. Conversion and selectivity measurements were performed every 20 °C, over a temperature range of 350−430 °C. Reaction product analysis was conducted using an on-line gas chromatograph (GC) (Interscience) that was equipped with a 50-m 100% dimethyl polysiloxane (BP1, ACHROM) column. A flame ionization detector (FID) was used, together with a micro-methanizer (Interscience) for detection of CO, CO_2, and all hydrocarbons that formed. Data evaluation was performed automatically by a macro written in Visual Basic under MS Excel.

Camille process control software from Argonaut, which regulated gas selection, gas flows, reactor temperature, valve selection, and GC operation, allowed us to automatically conduct the pretreatment and consecutive catalytic tests under different conditions. The reactor was permitted a period of 1 h for stabilization before sampling. The different microreactors were sampled sequentially—every 20 min, which corresponded to the analysis plus cooling time of the GC. It should be stressed that, under the present reaction conditions, the catalysts that were used did not deactivate.

Scaling-Up the Oxide Catalysts. The same sol−gel procedure was used for the large scale sol−gel synthesis. A detailed description is given elsewhere.[16] At the secondary screening stage, tests were performed in a continuous-flow gas-phase reactor that was equipped with four parallel reactors (4UPCFR), over a temperature range of 325−450 °C at atmospheric pressure.[16] Catalyst material (0.5 g, pelletized to a 0.125−0.250 mm fraction and diluted with 0.25 g of SiC of the same granule size) was packed between two layers of quartz wool. The molar feed composition was 3 parts isobutane, 1 part oxygen, and 2 parts helium, with a total flow rate of 40 mL/min, corresponding to a space time of $W/F_0 = 188$ mg s/mL per reactor. The sol−gel catalysts that were 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. Feed and products were analyzed with an on-line GC system (Hewlett−Packard, model HP 5890 Series II) equipped with (i) a CP WCOT fused silica column connected to a methanizer and an FID, and (ii) a molecular sieve 5 Å column that was connected to a thermal conductivity detector (TCD).

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