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Chemical Engineering Journal 82 (2001) 3–11

Chemical Engineering Journal

www.elsevier.com/locate/cej

High-throughput synthesis and screening of catalytic materials Case study on the search for a low-temperature catalyst for the oxidation of low-concentration propane

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Received 20 July 2000; accepted 24 October 2000

Abstract

Low-temperature catalysts for the total combustion of low-concentration propane in air have been searched for applying a combinatorial approach including an optimization procedure based on a genetic algorithm. A 1st generation of catalysts was prepared by impregnation of TiO_2 and Fe_2O_3 materials with randomly mixed solutions of eight individual compounds ($H_2[PtCl_6]\cdot xH_2O$, $(NH_4)_2PdCl_6$, $RhCl_3\cdot 2H_2O$, $RuCl_3\cdot H_2O$, $H[AuCl_4]\cdot 3H_2O$, Ag lactate, $Cu(NO_3)_2$, $Mn(NO_3)_2$) considered as potential catalytic compounds. After parallel testing of the 1st generation of the catalytic materials applying high-throughput testing equipment the most active catalysts were chosen to create a 2nd and after its testing a 3rd generation, respectively. A genetic algorithm was applied to set the compositions of the catalytic compounds of the 2nd and 3rd generation. Fe_2O_3 was not used as support for the succeeding generations since it lead to significantly inferior catalytic performances than TiO_2. The optimization strategy led to improved catalysts. Most of the final material converted propane to CO_2 at 150°C, the best ones oxidized propane even at 50°C.

Furthermore, the goal was pursued to compare the performance of two different high-throughput testing equipments. In both cases the ranking of 45 catalysts was nearly the same. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Combinatorial catalysis; High-throughput screening; Heterogeneous catalysts; Genetic algorithm for optimization; Evolutionary strategy

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1. Introduction

For special purposes such as air liquefaction for oxygen and nitrogen separation removal of gaseous hydrocarbons such as propane is required to avoid its dangerous condensation into liquid oxygen. The concentration of propane in air is usually in the order of significantly less than 1000 ppm. One alternative for propane removal is its total oxidation at low-temperatures (50–200°C) to CO_2 which can be easily separated from air before liquefaction by adsorption. There is, however, only little information available on the low-concentration and low-temperature total oxidation of propane.

For the total oxidation of hydrocarbons many different catalysts have been tested, most of them noble metals of the platinum group [1–7]. Pd and Pt are frequently used as primary elements whereas Rh, Ru, Os and Ir are applied as secondary metals in alloys because they are not stable at high-temperatures employed for most total oxidation catalyst applications [1]. Besides platinum metals transition metal oxides [1–3,8], perovskite-type oxides [1,2,9], metal-doped zeolites [10], metal-doped solid super acids [11] and highly dispersed Au catalysts [12] are active in total oxidation. A correlation between total oxidation activity and the metal–oxygen bond energy shows that the most active catalysts Pt, Pd, Ag_2O, Co_3O_4, CuO and MnO_2 have bond energies in the range of 40–250 kJ/mole [2]. However, to the authors knowledge, no catalyst is known which oxidizes hydrocarbons already at temperatures below 150°C or even at ambient temperature [13].

The best catalysts reported for combustion of propane seem to be Pt and Pd. Yu Yao investigated propane oxidation in the temperature range from 200 to 500°C and found Pt to be a better catalyst than Pd and Rh [4]. Similar results were obtained in Moro-oka et al. [3] and in Hodnett and co-workers [7], who found that the reaction starts at 150°C over a Pt/β-zeolite catalyst. Maier and co-workers [6], however, found that Pd is more active in comparison to Pt for C_1–C_3 alkane combustion whereas for oxidation of higher hydrocarbons Pt is the most active catalyst. Transition metal

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PII: S1385-8947(00)00348-X

oxides oxidize propane at 250°C or higher temperatures [8].

Against the above background it was the aim of our study to apply a combinatorial strategy and high-throughput synthesis and testing of catalytic materials for total propane oxidation in a lower temperature range from 50 to 200°C. For catalyst optimization an evolutionary strategy was used which has been described earlier [14]. Moreover, the comparative performance of two high-throughput catalytic testing equipments was studied. In one case, a multi-tubular reactor module (15 quartz tubes; d_{internal}, 3.5 mm; m_{cat}, 200 mg) charged with 250–500 μm particles [15,16], in the other case an array microreactor with 80 channels each containing one pellet (4 mm diameter by 1 mm high) [17] was used.

2. Combinatorial approach and catalyst optimization

Using a combinatorial strategy with an inherent optimization procedure [14] eight primary elements were combined randomly. The following steps were implied.

2.1. 1st step: initialization of the 1st generation of catalytic materials based on the predefined primary components

The composition of two libraries (1st generation) of 60 titania-supported catalytic materials and 60 materials based on α-Fe_2O_3 as support was set up of mixtures of Pd, Rh, Au, Mn, Cu, Pt, Ru and Ag of different quantitative and qualitative compositions. The compositions of the different materials of the two 1st generations were created in a stochastic manner in such a way that each catalytic material consisted of up to three of eight primary components.

2.2. 2nd step: parallel preparation and testing of catalytic materials of the 1st generation, evaluation of catalyst quality

The catalytic materials were synthesized and then tested for their catalytic performance in parallel according to the methods described in Section 3.

2.3. 3rd step: creation of the 2nd generation based on the catalytic results of the 1st generation

A population size of 45 materials based on the carrier material titania was used in the 2nd and 3rd generations using only TiO_2 as support since Fe_2O_3 proved not to be suited. The 2nd generation of catalytic materials was synthesized based on the most active materials of the 1st generation applying evolutionary operators (mutation, cross-over). The general description of the mutation and cross-over procedures has been reported elsewhere [14]. For the present study, the number of materials created by different operators was adjusted by the control parameters $A = 0.5$ and $B = 0.5$ determining the influence of each of the operators (cross-over, quantitative or qualitative mutation) on the optimization process (see [14]).

2.4. Subsequent steps: repetition of the 2nd and 3rd step for the subsequent generations

After some generations an approximate optimum is usually found and the catalyst compositions become similar.

3. Experimental

3.1. Catalyst preparation

The catalytic materials were prepared in parallel by the incipient wetness method using an automatic liquid handler (Gilson 215) which was controlled by a software code developed in-house [15]. The qualitative and quantitative loading of the carrier materials TiO_2 (Degussa Aerolyst 7710, 0.25–0.5 mm, $S_{\text{BET}} = 49\,\text{m}^2/\text{g}$, pore volume 0.88 ml/g) or α-Fe_2O_3 (0.25–0.5 mm, $S_{\text{BET}} = 57\,\text{m}^2/\text{g}$, pore volume 0.49 ml/g) amounted to 3 wt.% of up to five of eight active components (Pt, Pd, Rh, Ru, Au, Ag, Cu and Mn). The composition was established according to the above described procedure. The amounts of the aqueous metal–salt solutions in the required concentrations were supplied to the various vials. The following compounds were used in the preparation ($H_2[PtCl_6]\cdot xH_2O$, $(NH_4)_2PdCl_6$ (heated up to 100°C to convert to the better soluble Pd(II) salt), $RhCl_3\cdot 2H_2O$, $RuCl_3\cdot H_2O$, $H[AuCl_4]\cdot 3H_2O$ and Ag lactate (solved in a mixture of lactic acid and water), $Cu(NO_3)_2$, $Mn(NO_3)_2$). Stock solutions of high-concentrations were prepared from this compounds. Subsequently, the solutions were diluted and mixed by the automatic liquid handler and the carrier material samples which were located in an array of vials were impregnated with the appropriate solution. Since it was not possible to mix all solutions without any precipitation reactions the carrier material was loaded with the active components in three steps: (i) Ag (ii) mixture of Pt, Au, Mn, Cu and (iii) mixture of Pd, Rh, Ru. In the 3rd generation, where most of the catalysts contained ruthenium, it was added as $RuCl_3$ separately in the final preparation step. The precursor materials were dried after each step at 110°C for 4 h. All dried precursors were calcined in air (33 ml/min for 0.2 g catalyst) at 400°C for 2 h and reduced in hydrogen (33 ml/min for 0.2 g catalyst) at 250°C for another 2 h in the multi-tubular reactor or in the array microreactor, respectively.

3.2. Catalytic testing in the multi-tubular reactor module

For fast testing a 15-tubes reactor module was used which allowed to test up to 15 catalytic materials in a pseudo-parallel manner [15,16]. A premixed gas (0.1% propane, 20% O_2, 0.1% Ne used as internal standard, He balance) supplied by a mass flow controller was fed via a 16-port-valve either to a bypass or to one of the 15 reactors (quartz, i.d. 3.5 mm), at a time. The reactors which were immersed into a heated stainless steel block were consecutively operated. Through all the other reactors an inert gas was then passed. The reaction products of the selected reactor were passed to a quadrupole mass spectrometer (OMNISTAR, Balzers Instruments) through another 16-port-valve. The whole equipment was PC-controlled, thus all materials were automatically tested. The intensity of mass unit 43 characteristic for propane was measured until a steady state was reached; then, the final analysis of the composition of the effluent gas was performed and the degree of propane conversion was estimated from the intensities of mass 43 in the effluent and the bypass gas stream. Afterwards, the valves switched to the bypass and to the next reactor, this procedure was repeated until all materials positioned in the module had been tested. The test of one catalyst including bypass analysis consumed ca. 10–15 min, thus 15 catalysts could be tested at different reaction temperatures in 1 day.

3.3. *Catalytic testing in the multi-channel pellet reactor module*

The performance of the different generations of catalytic materials was assessed in arrays of parallel channel microreactors [17]. Each array contained 20 channels (1 mm × 1 mm) each with a cylindrical well (4 mm diameter by 1 mm high) to accommodate the catalytic material as a pellet. Thus, it was possible to test up to 80 catalytic materials simultaneously. The reactor arrays were stacked and placed inside a stainless steel heating block. Individual microreactor arrays were also fitted with dedicated electronic mass flow controllers to separately adjust the gas flow rates. However, in the present set of experiments feed gas flow rates were maintained the same for each array. Feed lines pass through a pre-heater system that was also machined from stainless steel. The temperatures of the array microreactors and the pre-heat section were regulated with the use of electrical heating cartridges and thermocouples inserted into the stainless steel blocks and PID controllers (Omega, Stamford CT).

The reactor system was mounted on a stand that was part of a high precision, computer controlled *x–y–z* movement mechanism. Catalyst testing proceeded in the following manner. First, all of the catalytic pellets, together with selected duplicates and blanks, were placed into the wells of the microreactors. The reactor was then heated to the desired operating temperature under the flow of argon gas. Upon reaching the set point temperature, the gas flow was switched to reactants.

Catalyst screening was accomplished by withdrawing a small stream (about 1 cm^3/min) from each microreactor channel effluent using a 50 μm diameter capillary sampling probe, followed by gas analysis using quadrupole mass spectrometry (Leybold). The probe was kept in each reactor channel for a period of 5–15 s to acquire multiple mass spectrometric scans, after which it was rapidly moved to the next channel. Consequently, it was possible to screen the entire 80 catalyst library in a time period of 7–20 min. Mass 43 was monitored to ascertain the activity of the catalyst.

4. Results and Discussion

4.1. *Results obtained by the multi-tubular reactor module*

In the introductory experiments in the multi-tubular reactor module 15 catalysts were tested at five reaction temperatures: 25, 50, 100, 150 and 200°C. At 25°C only low conversions of propane were measured while at 200°C some catalysts showed complete conversion. Thus, neither the lowest nor the highest temperatures were considered to be suitable for ranking catalyst activities. With some catalysts 100% conversion was reached even at 150°C but these catalysts deactivated fast which was probably due to an inhibiting effect of adsorbed water. Therefore, all the subsequent testing was carried out between 50 and 150°C and propane conversion at 100°C after reaching a steady state was chosen to assess the various catalytic materials.

The catalyst compositions and the results of testing the 1st catalyst generation based on TiO_2 as carrier material are summarized in Table 1. The assessment of the composition of the 10 most active materials of this generation showed that seven of these materials contained Ru and that Pd was present in five catalysts. For the 10 most inactive catalysts, Ru was present in only two catalysts whereas seven samples contained Pd and six samples contained Ag. As a first conclusion one could assume that Ru is an active element in the low-temperature total oxidation of propane. The catalytic tests of the catalysts supported on α-Fe_2O_3 showed very poor activities. In this case, propane conversions were below 10% even at 150°C, therefore Fe_2O_3 was excluded as a support in the subsequent generations and only TiO_2 was used as carrier material. The TiO_2-supported catalysts of the 1st generation were ordered then by their activity, by using the genetic algorithm the compositions of 45 materials of the 2nd generation were derived.

The composition and the results of the catalytic tests of the 2nd generation of catalytic materials are given in Table 2. In contrast to the randomly composed 1st generation, in which 38% of all catalysts contained Ru, it is now present in 51% of all the catalysts. The best catalytic materials of the 2nd generation showed slightly higher activities than the best materials of the 1st generation (Fig. 1). It is evident that the most active materials contain a relatively high amount of Ru running between 0.8 and 2 wt.%. All inactive catalysts, however, contain no or only traces (<0.1 wt.%) of Ru.

Table 1
Metal contents (wt.%) and catalytic results (propane conversion degrees) of the TiO_2 catalysts of the 1st generation (ordered by conversion at 100°C): 200 mg catalyst, feed: 0.1% propane, 20% O_2, 0.1% Ne (internal standard), He balance, gas flow rate 6 $cm^3\,min^{-1}$

Catalyst	Pt	Pd	Rh	Ru	Au	Cu	Ag	Mn	X (%); 50°C	X (%); 100°C	X (%); 150°C
I/1	0.69	–	–	1.24	–	–	1.06	–	10	27	63
I/2	–	–	1.10	1.00	0.91	–	–	–	5	24	65
I/3	–	1.53	–	1.40	–	0.08	–	–	0	22	73
I/4	–	–	0.83	1.44	–	–	–	0.73	4	21	55
I/5	–	0.99	–	1.17	–	–	–	0.84	5	21	61
I/6	0.49	1.04	–	–	–	–	–	1.47	0	20	62
I/7	–	0.60	–	1.22	–	–	1.19	–	1	19	63
I/8	–	1.35	–	1.13	–	0.52	–	–	3	17	53
I/9	–	–	–	–	1.62	–	0.73	0.65	2	17	44
I/10	–	0.07	–	–	1.71	1.21	–	–	2	16	51
I/11	1.02	–	0.52	–	1.45	–	–	–	2	16	42
I/12	–	1.15	1.00	0.84	–	–	–	–	2	14	49
I/13	–	0.01	–	1.31	–	–	1.67	–	0	11	51
I/14	–	–	0.44	1.06	–	1.50	–	–	0	10	48
I/15	–	–	2.58	0.17	0.24	–	–	–	0	10	38
I/16	–	2.88	–	0.06	–	–	–	0.05	2	8	29
I/17	0.66	–	0.01	–	–	–	2.33	–	1	8	33
I/18	–	–	–	1.11	–	–	1.06	0.83	0	8	33
I/19	–	1.38	–	0.09	1.52	–	–	–	2	7	22
I/20	0.26	–	–	1.51	1.22	–	–	–	3	5	32
I/21	0.99	1.98	–	0.03	–	–	–	–	1	5	11
I/22	0.98	–	–	–	–	0.97	1.04	–	0	5	28
I/23	0.24	–	–	–	–	1.03	1.73	–	4	5	9
I/24	1.57	–	–	0.33	–	–	–	1.10	1	5	21
I/25	0.38	2.53	0.09	–	–	–	–	–	1	4	19
I/26	–	–	1.77	–	0.04	1.19	–	–	1	4	2
I/27	1.28	–	–	0.26	–	–	1.46	–	3	4	27
I/28	–	–	1.66	–	–	–	0.15	1.18	2	4	12
I/29	–	1.21	1.33	–	–	0.45	–	–	3	4	9
I/30	–	1.91	–	–	1.07	0.02	–	–	1	3	12
I/31	–	1.16	–	–	–	–	0.20	1.63	0	3	6
I/32	–	–	–	1.06	1.07	0.87	–	–	0	3	9
I/33	2.37	–	–	–	0.37	0.26	–	–	2	3	11
I/34	–	1.53	–	–	–	1.09	0.38	–	2	2	5
I/35	–	0.70	1.42	–	–	–	0.88	–	0	2	10
I/36	–	–	–	–	–	1.10	1.01	0.89	3	2	4
I/37	–	–	–	0.32	–	0.67	–	2.01	2	2	3
I/38	0.58	–	–	–	1.78	–	0.64	–	2	2	2
I/39	1.10	0.65	–	–	1.24	–	–	–	1	2	11
I/40	–	0.84	1.58	–	–	0.58	–	–	1	2	4
I/41	–	–	–	0.75	–	0.51	1.73	–	2	2	27
I/42	0.91	–	0.94	–	1.15	–	–	–	1	2	0
I/43	–	1.11	–	–	1.40	–	0.48	–	0	2	3
I/44	–	–	–	–	0.89	1.17	–	0.94	2	2	2
I/45	0.03	0.83	–	–	–	–	2.14	–	1	1	1
I/46	0.48	1.03	–	–	–	–	1.49	–	1	1	1
I/47	1.32	0.07	1.60	–	–	–	–	–	1	1	2
I/48	–	1.30	1.10	–	–	0.60	–	–	1	1	11
I/49	–	1.42	1.51	–	–	0.06	–	–	0	1	0
I/50	–	–	1.83	–	–	–	0.64	0.53	2	1	4
I/51	1.12	–	1.67	–	0.22	–	–	–	0	1	10
I/52	–	–	–	–	–	1.11	0.69	1.20	1	1	2
I/53	0.83	–	1.42	–	–	0.75	–	–	1	1	7
I/54	–	1.13	–	1.79	0.09	–	–	–	2	0	5
I/55	–	–	1.94	–	–	–	0.40	0.66	0	0	9
I/56	–	0.17	1.04	1.79	–	–	–	–	2	0	0
I/57	–	–	–	–	1.32	0.46	–	1.23	1	0	0
I/58	–	0.83	0.90	–	–	–	1.27	–	0	0	7
I/59	–	–	0.74	–	–	0.29	1.97	–	1	0	5
I/60	–	0.81	–	–	1.17	–	–	1.02	0	0	2

Table 2
Metal contents (wt.%) and catalytic results (propane conversion degrees) of the TiO_2 catalysts of the 2nd generation (ordered by conversion at 100°C): 200 mg catalyst, feed: 0.1% propane, 20% O_2, 0.1% Ne (internal standard), He balance, gas flow rate 6 $cm^3\,min^{-1}$

Catalyst	Pt	Pd	Rh	Ru	Au	Cu	Ag	Mn	X (%); 50°C	X (%); 100°C	X (%); 150°C
II/1	1.07	–	–	1.92	–	–	–	–	2	29	70
II/2	–	0.99	–	2.01	–	–	–	–	1	29	62
II/3	–	–	1.09	1.91	–	–	–	–	1	24	60
II/4	0.18	–	0.99	1.01	0.82	–	–	–	1	24	56
II/5	0.89	1.07	0.06	0.98	–	–	–	–	2	22	58
II/6	0.39	–	–	1.4	–	–	1.2	–	3	20	56
II/7	–	–	–	2.05	–	0.95	–	–	1	20	58
II/8	–	–	0.84	0.77	1.39	–	–	–	4	18	47
II/9	0.2	–	–	1.11	0.9	–	0.79	–	2	16	52
II/10	0.84	–	–	1.51	–	–	0.65	–	1	16	51
II/11	0.39	–	–	1.4	–	–	1.2	–	1	14	61
II/12	–	–	0.89	0.81	0.74	0.55	–	–	1	10	39
II/13	–	0.91	0.58	1.01	–	–	–	0.51	0	9	43
II/14	–	–	–	0.49	–	0.33	1.12	1.06	1	5	26
II/15	–	–	–	0.41	–	–	–	2.59	1	3	30
II/16	–	–	1.97	–	–	1.03	–	–	3	3	7
II/17	0.8	1.47	–	0.17	–	–	–	0.56	2	3	14
II/18	2.52	–	–	–	0.48	–	–	–	1	3	7
II/19	1.76	–	–	–	–	–	–	1.24	1	3	4
II/20	–	2.96	–	0.04	–	–	–	–	1	2	13
II/21	–	0.71	1.45	0.05	0.79	–	–	–	2	2	8
II/22	–	–	1.94	–	–	1.06	–	–	1	2	7
II/23	–	–	1.26	–	0.94	–	0.43	0.38	2	2	5
II/24	–	2.96	–	0.04	–	–	–	–	2	2	4
II/25	–	2.4	–	–	–	–	0.6	–	3	2	2
II/26	0.58	1.29	0.3	–	0.83	–	–	–	2	2	5
II/27	–	2.55	–	–	–	–	0.45	–	0	1	2
II/28	–	–	2.08	0.14	0.2	–	–	0.59	0	1	16
II/29	–	–	1.41	–	0.69	–	0.49	0.41	0	1	1
II/30	–	–	1.79	–	–	1.21	–	–	3	1	7
II/31	0.61	–	–	–	–	0.59	0.65	1.15	1	1	1
II/32	–	2.19	–	–	–	0.81	–	–	2	1	5
II/33	0.17	–	0.92	–	–	0.71	1.19	–	0	1	1
II/34	–	0.7	–	0.05	0.77	–	1.48	–	0	1	2
II/35	0.37	–	–	–	–	1.32	1.3	–	1	1	1
II/36	0.75	1.43	–	–	0.8	0.02	–	–	2	1	4
II/37	–	–	1.18	–	0.88	–	0.11	0.83	1	1	5
II/38	1.88	1.12	–	–	–	–	–	–	1	1	5
II/39	–	1.67	–	0.04	1.26	–	–	0.03	1	1	4
II/40	0.36	–	–	–	–	–	2.64	–	0	0	2
II/41	–	0.07	–	–	1.63	1.15	0.15	–	0	0	1
II/42	–	–	1.76	–	–	–	–	1.25	1	0	3
II/43	–	–	–	–	–	1.66	–	1.34	0	0	0
II/44	0.18	–	–	–	–	0.8	1.33	0.68	0	0	0
II/45	–	2.07	–	0.04	–	–	0.85	0.04	1	0	0

In the 3rd generation most of the catalytic materials (80%) contain Ru (Table 3). Many catalysts containing a large amount of Ru show a high total oxidation activity for propane. On the other side, all catalysts containing no Ru or only traces (<0.1 wt.%) are nearly inactive. Fig. 1 shows the dramatic increase of the catalytic activity in the 3rd generation.

In addition to the results described, an attempt was made to further identify the most active catalytic metal by a "non-combinatorial procedure". Eight TiO_2 catalysts were prepared which contained 3 wt.% of only one element (Ru, Rh, Pd, Pt, Au, Cu, Ag and Mn). The results of these catalytic tests are summarized in Fig. 2. The most active of the eight elements is Ru as already derived from the three generations. Rh and Pt show a moderate activity whereas the other metals were nearly inactive in propane oxidation. The "non-combinatorial procedure" also gives the result that Ru is a very active element in deep oxidation of propane. However, the best catalysts derived from the combinatorial strategy are multi-component materials containing Mn, Au or metals of the platinum group as a second element besides Ru. These catalysts have

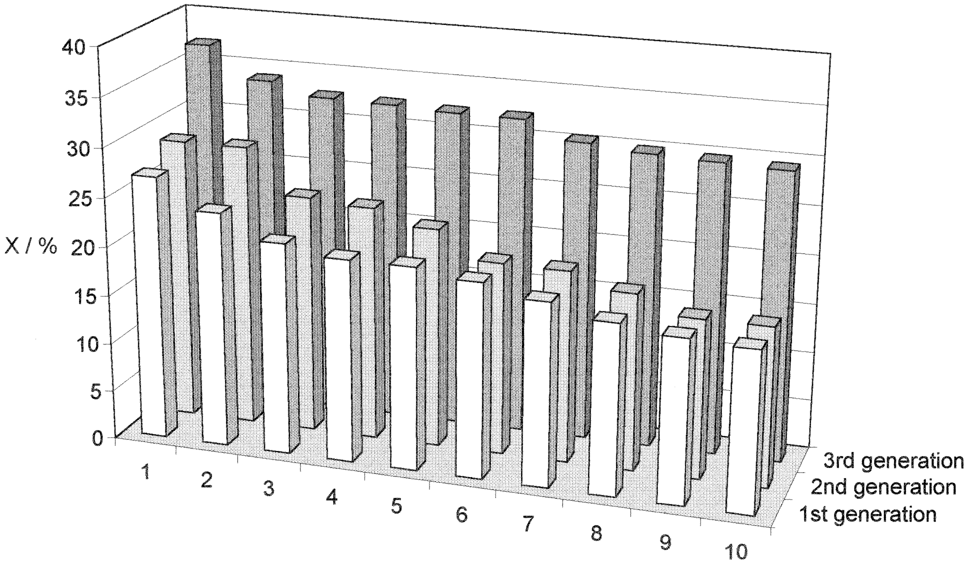

Fig. 1. Comparison of the most active materials of the three catalyst generations tested in the multi-tubular reactor module: 200 mg catalyst, feed: 0.1% propane, 20% O_2, 0.1% Ne (internal standard), He balance, gas flow rate 6 $cm^3 min^{-1}$.

an activity being up to 20% higher compared with the monometallic Ru catalyst. To find such a bimetallic optimum composition including variations of quantitative compositions much more materials would have been required by a "non-combinatorial procedure" than by the procedure applied in this work.

The extraordinary activity of the Ru catalysts may be caused by the ability of the carrier material TiO_2 to stabilize Ru in its metallic state even in the presence of oxygen as detected by XPS studies [18,19].

4.2. Results obtained by the array microreactor module and comparison with those of the multi-tube microreactor module

To compare the two different testing equipments the 3rd catalyst generation was also tested in the array microreactor [17]. Caused by the construction of this reactor a minimum gas flow rate of 6 $cm^3 min^{-1}$ and catalyst pellets of 20 mg each had to be used and thus, the space velocity is 10 times higher compared with the multi-tube reactor. Therefore, to

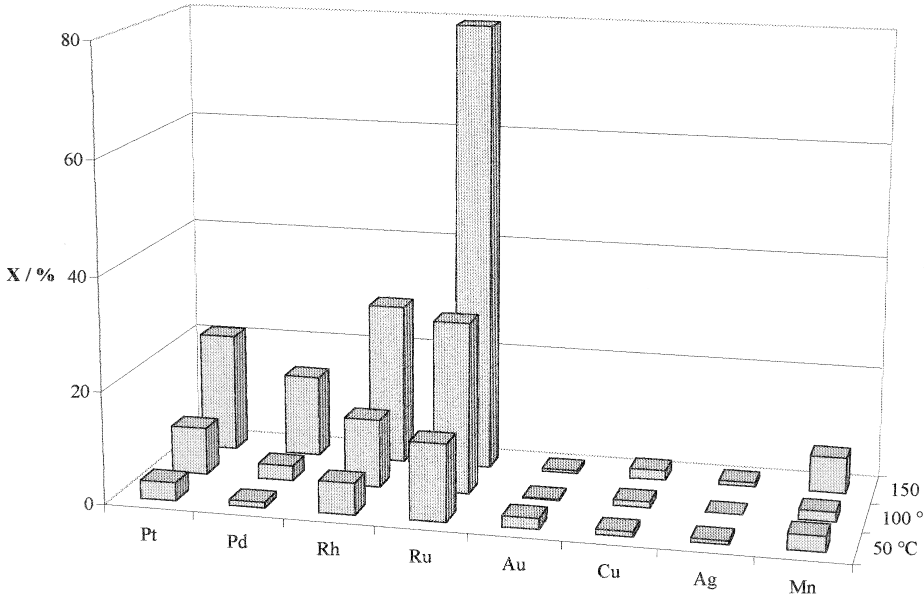

Fig. 2. Catalytic results (propane conversion degrees) of TiO_2 catalysts containing 3 wt.% of pure metals on TiO_2 tested in the multi-tubular reactor module: 200 mg catalyst, feed: 0.1% propane, 20% O_2, 0.1% Ne (internal standard), He balance, gas flow rate 6 $cm^3 min^{-1}$.

Table 3
Metal contents (wt.%) and catalytic results (propane conversion degrees) of the TiO_2 catalysts of the 3rd generation (ordered by conversion at 100°C): 200 mg catalyst, feed: 0.1% propane, 20% O_2, 0.1% Ne (internal standard), He balance, gas flow rate $6\,cm^3\,min^{-1}$[a]

Catalyst	Pt	Pd	Rh	Ru	Au	Cu	Ag	Mn	Multi-tube reactor			Array microreactor module					
									50°C	100°C	150°C	100°C	150°C	175°C	200°C	225°C	250°C
III/1	–	–	–	1.72	–	–	–	1.28	11	37	84	4	11	30	55	76	85
III/2	0.65	–	–	2.35	–	–	–	–	7	34	84	0	6	16	50	77	89
III/3	–	–	1.10	1.00	0.91	–	–	–	12	33	68	2	7	12	29	60	76
III/4	–	–	1.60	1.40	–	–	–	–	12	33	68	−3	0	0	25	58	77
III/5	–	0.59	–	2.41	–	–	–	–	4	32	81	−4	17	27	52	73	85
III/6	1.07	–	–	1.93	–	–	–	–	9	32	83	3	12	24	47	71	84
III/7	–	–	–	1.66	1.34	–	–	–	10	31	80	2	14	9	43	74	88
III/8	0.20	–	1.15	1.17	0.47	–	–	–	16	30	70	3	1	12	24	57	80
III/9	0.24	–	0.76	1.33	–	–	–	0.67	9	30	60	4	8	11	30	65	82
III/10	–	–	–	3.00	–	–	–	–	12	30	75	−1	19	26	64	85	90
III/11	0.20	–	1.15	1.17	0.47	–	–	–	4	30	67	0	6	13	31	74	84
III/12	0.65	–	–	2.35	–	–	–	–	15	29	78	3	7	17	38	75	90
III/13	0.21	–	1.19	0.61	0.99	–	–	–	12	29	67	1	4	3	14	46	69
III/14	0.24	–	1.36	1.39	–	–	–	–	13	28	59	−1	2	8	21	60	82
III/15	–	1.49	–	1.52	–	–	–	–	9	28	58	1	1	7	15	48	72
III/16	–	–	1.57	1.43	–	–	–	–	2	25	72	−3	12	23	33	71	83
III/17	–	1.29	–	0.98	0.72	0.02	–	–	7	22	51	2	3	10	14	42	61
III/18	–	0.79	0.68	0.58	0.95	–	–	–	3	22	66	−4	3	7	12	45	64
III/19	–	–	0.43	0.75	1.44	–	–	0.38	1	20	58	1	7	12	32	57	76
III/20	0.15	–	0.84	0.86	0.69	0.47	–	–	1	20	55	1	10	7	22	44	66
III/21	–	0.01	0.72	1.00	–	–	1.27	–	5	18	43	1	1	8	26	50	70
III/22	–	–	–	1.52	–	–	1.48	–	8	18	59	2	8	10	27	63	77
III/23	–	–	0.88	2.12	–	–	–	–	12	18	57	1	24	28	51	76	85
III/24	0.51	–	0.80	0.91	–	–	0.78	–	2	16	51	−1	9	15	24	55	72
III/25	0.10	–	–	0.56	0.45	–	0.39	1.49	4	15	43	6	0	9	12	33	55
III/26	0.49	–	–	1.76	–	–	0.75	–	7	14	67	7	5	9	26	61	78
III/27	0.59	–	–	1.22	–	0.57	0.62	–	2	14	47	−1	11	20	25	57	75
III/28	0.55	–	–	0.98	–	1.47	–	–	6	14	50	−11	7	16	10	44	67
III/29	–	–	1.91	0.13	0.18	–	0.78	–	4	14	26	−1	1	4	−2	8	28
III/30	0.26	–	–	0.91	–	–	0.78	1.06	1	13	49	0	6	12	34	57	73
III/31	–	0.01	–	0.82	–	–	1.04	1.13	8	13	50	0	7	13	18	41	60
III/32	–	–	0.77	0.71	0.64	0.47	0.41	–	5	13	38	3	3	6	10	31	58
III/33	–	–	2.14	0.15	0.20	–	–	0.52	5	13	20	−2	0	−3	7	7	24
III/34	0.70	0.01	–	1.01	–	–	1.29	–	5	11	43	−2	2	3	23	54	74
III/35	–	1.08	0.65	0.07	1.19	–	–	–	3	7	21	2	0	−4	−5	0	1
III/36	–	–	1.60	–	–	–	–	1.40	4	3	7	1	−6	5	1	13	17
III/37	1.52	–	–	–	–	1.49	–	–	4	2	3	2	2	2	8	−4	10
III/38	–	0.59	0.71	0.04	0.65	1.00	–	–	0	2	9	−5	4	8	−7	5	9
III/39	–	0.05	–	–	1.27	0.90	0.78	–	1	2	1	0	−1	1	−3	6	8
III/40	–	2.55	–	–	–	–	0.45	–	0	1	5	0	−7	−2	−7	−1	3
III/41	0.32	0.68	–	–	–	1.05	–	0.95	0	1	3	3	−2	−5	−1	1	1
III/42	1.19	–	–	–	–	–	1.82	–	1	1	1	0	0	0	−3	0	7
III/43	1.46	–	–	–	–	–	1.55	–	1	0	0	4	−6	−2	3	5	5
III/44	–	–	–	–	–	3.00	–	–	0	0	0	−4	5	12	−3	1	−4
III/45	–	–	–	–	1.22	0.73	0.55	0.49	1	0	1	−2	0	3	−1	5	7

[a] The negative numbers represents the error in determining small propane conversion degrees.

reach similar degrees of propane conversion, higher temperatures had to be applied. Table 3 summarizes the testing results of the 45 catalysts of the 3rd generation obtained by the two screening equipments: the catalysts are ordered by their activities at 100°C measured by using the multi-tubular reactor. In the array microreactor module very low conversions were achieved below 150°C caused by the high space velocity so that a comparison of the catalyst activities at this temperature is nearly impossible. Better conditions for catalyst comparison and ranking were temperatures between 175 and 250°C resulting in conversions in the range from 20 to 90% for the best performing catalysts.

In Fig. 3 the results obtained in both screening equipments are compared at reaction conditions at which the best catalysts show nearly 90% conversion degree. It is obvious that the most active catalysts could be detected by both test-

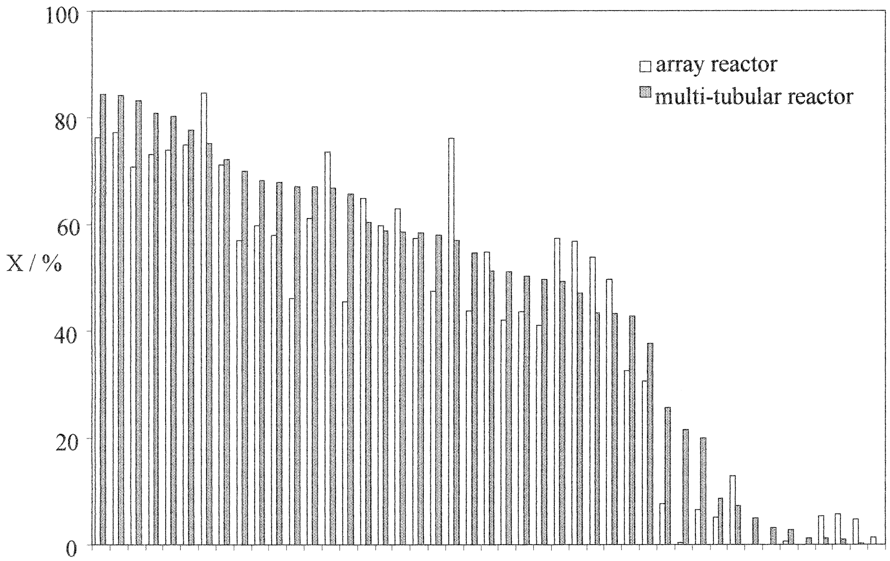

Fig. 3. Comparison of the testing results of catalysts of 3rd generation obtained by the multi-tubular reactor at 150°C and the array reactor module at 225°C ordered by propane conversion in the multi-tubular reactor at 150°C.

ing systems. Similarly, the same catalysts were found to be nearly inactive for deep oxidation of propane.

5. Conclusions

Summarizing, it is concluded that Ru is the most active element in the low-temperature total oxidation of propane among catalytic materials tested, followed by Rh, Pt and Pd. Catalysts which contain high amounts of Ru on TiO_2 as support are able to convert propane of low-concentration in air to CO_2 at 150°C, and can oxidize part of the propane even at 50°C. Furthermore, it has been shown that by using a genetic algorithm the composition of multimetal catalysts can be optimized. Looking at the composition of the most active catalysts, by replacing part of Ru by the elements Pt, Pd, Rh, Au or Mn the activity of the catalyst can be increased in comparison to the monometallic Ru catalyst. However, a minimum content of 1 wt.% Ru is necessary for an active catalyst.

From a fundamental point of view it will be interesting to study the effect of catalyst composition as well as its bulk and surface structure on activity.

By comparing the testing results of the two screening equipment it was shown that by using the multi-tubular reactor module 15 catalysts could be tested under conditions similar to that in fixed-bed lab reactors at different temperatures in 1 day giving reproducible quantitative results. With the array microreactor module catalyst libraries can be tested even faster. Although, the analytical accuracy of the obtained conversion degrees was lower as compared to the multi-tubular reactor module, the most active and the inactive catalysts from the libraries containing all together 150 catalytic materials could be found in a rather short period of time.

Acknowledgements

The authors thank Dr. Ulrich Schülke for preparation of Fe_2O_3 carrier material and Peter Ignaszewski and Martin Lucas for technical assistance, and Kevin Krantz and Sukru Ozturk with the array channel microreactor experiments. Financial support by the German Federal Ministry of Education and Research (contract no. 03D0068D0) is gratefully acknowledged.

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