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Ethylene and propene by oxidative dehydrogenation of ethane and propane
‘Performance of rare-earth oxide-based catalysts and development of redox-type catalytic materials by combinatorial methods’

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Abstract

Selected aspects related to the mode of reactor operation and to the development of catalysts for the oxidative dehydrogenation of ethane and propane to their respective olefins are dealt with. The differences in the catalytic conversion when applying ethane or propane on rare-earth-oxide (REO)-based catalysts leading to the ignition of the reaction mixture are discussed. For ethane dehydrogenation, ethylene yields up to 46% were achieved by non-isothermal operation. Non-isothermicity was caused by ignition of the reaction and the resultant heat production. The formation of ethylene occurred via thermal pyrolysis and oxidative dehydrogenation. In general, autothermal operation looks promising for the production of ethylene from ethane. The advantage of REO-based catalysts as compared to noble metals like Pt is their high thermal stability. There are, however, limitations regarding the dehydrogenation of propane to propene in the autothermal mode. A high propene yield is not possible when applying such conditions since C–C scission results in a decrease of propene selectivity. The search for new active and selective formulations operating at low temperatures is, therefore, still timely. Against this requirement, special attention was given to a combinatorial and evolutionary approach for the selection and optimization of catalytic materials for the oxidative dehydrogenation of propane; selected experimental results as a proof of principle are presented.

Keywords: Oxidative dehydrogenation of ethane and propane; Autothermal operation; Rare-earth-oxide-based catalysts; Redox catalysts; Catalyst optimization; Combinatorial catalysis; Evolutionary approach

1. Introduction

Much research effort is currently devoted to the chemical conversion of light alkanes to valuable chemicals. In particular, the increased demand for light olefins requires the development and understanding of new catalytic routes comprising novel catalytic materials and modes of operation. Existing commercial non-oxidative dehydrogenation processes imply strongly endothermic reactions and require large amounts of heat. Among the different reactor concepts and modes of operation which have been examined [1–12], autothermal processing looks attractive due to its high energy efficiency: the heat generated by reaction is used to sustain thermal reactions after ignition [1–6]. As proposed in [1–3], a complex interplay of catalytic and gas-phase reactions takes place in this case.

In the present contribution, the catalytic conversions of ethane and propane are compared when using a

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layer of REO-based catalyst for the ignition of the reaction mixture. The potential of autothermal processes for both ethane and propane is analyzed in general taking into account also literature data.

This paper also gives results on catalyst development for the oxidative dehydrogenation of propane. For this purpose, a combinatorial and evolutionary approach described in detail elsewhere [13] was used. The application of combinatorial methods for the discovery of new heterogeneous catalysts and the development of high throughput screening methods is a fast developing area [14–21]. Although only a few examples have been reported in the scientific literature up to now, there are indications that new high-tech screening techniques might become standard in the near future. In this context, concepts and tools regarding the creation of libraries of catalytic compositions are of high importance, in particular for multicomponent formulations. Different strategies may be used to generate and screen a large number of catalytic materials of different compositions and optimization methods comprising evolutionary algorithms appear promising. In the present work, a preliminary example is described to illustrate the application of the evolutionary approach for finding catalytic compositions from a broad basis of single redox compounds considered to be important for the oxidative dehydrogenation of propane.

2. Experimental

2.1. Catalysts

$SmSr_{0.2}O_x$ and $LaSr_{0.02}O_x$ catalysts were prepared by the addition of a strontium hydroxide solution to the respective lanthanide nitrate solution. The mixture was stirred and heated to evaporate the water. The dried sample was finally calcined in a flow of oxygen at 973 K for 2 h. Furthermore, a $SmNa_{0.028}P_{0.014}O_x$ catalyst was prepared by impregnation of Sm_2O_3 with a $Na_2HPO_4{\cdot}12H_2O$ solution. After drying at 120°C the catalyst was calcined in air at 700°C for 4 h.

For preparing redox catalysts used in the evolutionary procedure, the starting compounds (see below) containing the primary elements selected for any catalytic material were dispersed or dissolved in water. The mixture was stirred for 30 min at 80°C. The excess of water was evaporated while stirring at ca. 100°C; the remaining solid was then dried at 120°C for 10 h and finally calcined at 600°C for 3 h in air. Starting compounds were: NH_4VO_3 (Merck, p.a.), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Riedel de Haën, p.a.), $Mn(NO_3)_2{\cdot}4H_2O$ (Merck, p. a.), $Fe(NO_3)_3{\cdot}9H_2O$ (Fluka, p.a.), $Zn(NO_3)_2{\cdot}6H_2O$ (Merck, p.a.), Ga_2O_3 (Aldrich, 99.99 %), GeO_2, (Merck, >99.9%), Nb_2O_5 (Alfa, 99.9%), H_2WO_4 (Fluka, puriss.), $Co(NO_3)_2{\cdot}6H_2O$ (Merck, p.a.), $Ni(NO_3)_2{\cdot}6H_2O$ (Fluka, p.a.), $Cd(NO_3)_2{\cdot}4H_2O$ (Merck, p.a.), $In(NO_3)_3{\cdot}H_2O$ (Fluka, pract.).

2.2. Catalytic studies

Catalytic experiments on REO-based catalysts were carried out using an U-form quartz reactor ($Ø_{int} = 6$ mm for the catalyst (quartz) containing zone; $Ø_{int} = 2$ mm for the outlet tube) operated at ambient pressure and equipped with on-line gas chromatography. A quartz capillary ($Ø_{ext} = 3$ mm) containing a movable thermocouple for measuring the temperature profiles was placed in the reactor. The catalyst ($m_{cat} = 0.2$ g, $d_p = 250$–$355\,\mu$m) was packed between two layers of quartz particles of the same size. The oven was filled with sand in which the reactor was immersed for better insulation. After preheating the catalyst to 300°C in air, the reaction mixture consisting of C_2H_6 (C_3H_8), O_2 and N_2 was continuously passed over the catalyst at a total flow rate of 330 (220) ml/min (STP); the reactor was heated further to achieve the ignition detected as a fast temperature rise. After ignition the reactions were sustained due to the heat produced by oxidative reactions at the desired maximal temperature (T_R) in the catalyst bed; T_R was controlled by the preheated feed gas, the temperature of which was adjusted via the temperature of the sand bath. The partial pressure of ethane (or propane) was 45.5 (40) kPa and the ethane (or propane)-to-oxygen ratio was 2.5 (2).

To accelerate the catalytic testing when using the evolutionary catalyst development approach, six U-form reactors ($Ø_{int} = 6$ mm) made of quartz were operated in parallel at ambient pressure. To minimize temperature gradients, the reactors were immersed in a fluidized bed of sand of constant temperature. The reaction temperature was 500°C in all experiments. A reaction mixture consisting of propane, oxygen and nitrogen ($C_3H_8/O_2/N_2 = 2/1/2$) was passed through each bed of catalyst particles ($m_{cat} = 0.3$ g; $d_p = 250$–$355\,\mu$m); the total flow rates were varied from 10 to 100 ml/min (STP) to acquire selectivities at different degrees of conversion. On-line gas chromatography was used to analyze the feed and effluent compositions.

3. Results and discussion

3.1. Oxidative dehydrogenation of ethane and propane on REO-based catalysts

In our previous work [1,2], it was shown that adsorbed oxygen is involved in alkane activation on REO-containing catalysts and that the catalyst performance is determined by its activity towards oxygen adsorption. In the oxidative dehydrogenation of ethane (ODE) and propane (ODP) on REO-based catalysts, e.g. Ln_2O_3/SrO (Ln = Sm, La, Nd) and $Na\text{-}P/Sm_2O_3$, the ignition of the reaction mixture took place in continuous-flow operation using undiluted catalyst particles and fuel-rich conditions. After ignition, a sharp temperature increase occurred at the beginning of the catalyst layer; the temperature was then mostly well above 600°C, this being the border between catalytic and homogeneous gas-phase oxidation. Characteristic temperature profiles in the reactor are given elsewhere [1,2]. The heat produced by the oxidative reactions was sufficient for subsequent endothermic thermal pyrolysis which most probably takes place in the gas phase; this corresponds to autothermal operation.

A particular aim of the current contribution is to compare the catalytic behavior of REO-based catalysts regarding their use for the autothermal operation in the oxidative conversion of ethane and propane as well as to analyze the potential of the autothermal operation in general for obtaining the dehydrogenation products when using propane vs. ethane.

Selected results related to the best yields towards dehydrogenation products on REO based catalysts in both ethane and propane dehydrogenation are presented in Table 1. Under the conditions applied (see Section 2), the reactions were sustained after ignition due to the heat produced by oxidative reactions, this being characterized by the maximal temperature (T_R) measured in the catalyst bed with preheating of the feed gas, the temperature of which was 100–300°C lower than the maximum value. Reaction products were hydrocarbons and CO_x; no oxygenates were detected and oxygen conversions amounted to >98–99%. It should be noted that the achievement of the desired temperature was strongly determined by the reactor configuration and conditions applied. Under these circumstances, the ignition temperatures were similar for ethane and propane, ranging from 450 to 480°C for $SmSr_{0.2}O_x$ and $LaSr_{0.02}O_x$ catalysts and from 700 to 710°C for $SmNa_{0.028}P_{0.014}O_x$.

In the ODE, ethylene yields of 44–46% at conversions above 50% were obtained at short contact times of the order of 30–40 ms. For the ODP, olefins yields of 28–44% ($S = 56$–59%) were achieved at contact times of ca. 60 ms. Higher selectivities to C_2H_4 (ca. 36%) compared to C_3H_6 (ca. 20%) were observed over the whole range of reaction conditions for all the catalysts. The lower propene yield was due to C–C bond cleavage.

The effect of temperature on the alkane conversion and the product distribution is shown in Fig. 1 for both ODE and ODP. The variation of temperature in the catalyst layer was achieved by increasing the feed

Table 1
Catalytic performance of REO-based catalysts in the oxidative dehydrogenation of ethane and propane in continuous flow operation

Catalyst	Ethane[a]					Propane[b]					
	T_R (°C)	X (%)	Selectivity (%)			T_R (°C)	X (%)	Selectivity (%)			
			C_2H_4	CH_4	C_{3+}			C_3H_8	C_2H_4	CH_4	C_{3+}
$LaSr_{0.02}O_x$	800	46	64	5	2	735	57	20	36	14	5
$SmSr_{0.2}O_x$	855	52	66	6	3	710	50	20	36	11	4
$SmNa_{0.028}P_{0.014}O_x$	867	67	68	11	3	780	77	22	37	18	5

[a] $P_{C_2H_6} = 45.5\,\text{kPa}$, $P_{O_2} = 18.2\,\text{kPa}$, $m_{cat} = 0.2\,\text{g}$, $\tau = 0.036\,\text{g s ml}^{-1}$ (STP), $X(O_2) > 99\%$.

[b] $P_{C_3H_8} = 40\,\text{kPa}$, $P_{O_2} = 20\,\text{kPa}$, $m_{cat} = 0.2\,\text{g}$, $\tau = 0.06\,\text{g s ml}^{-1}$, $X(O_2) > 98\%$.

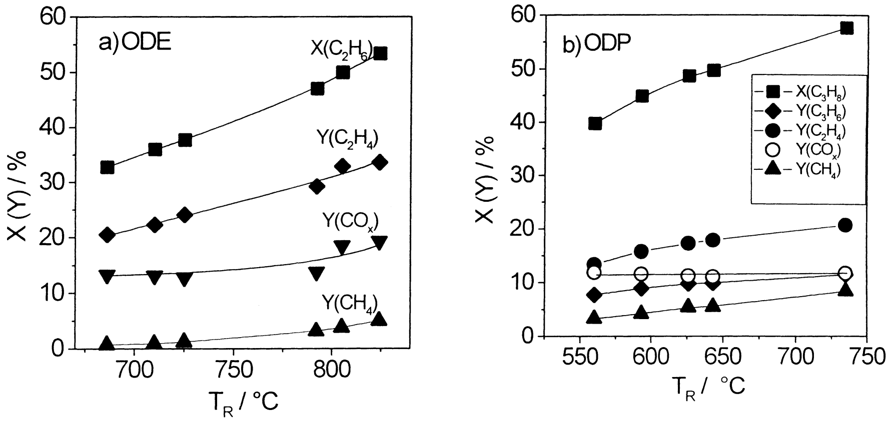

Fig. 1. Dependence of ethane (a) and propane (b) conversions and product yields on temperature for a $LaSr_{0.02}O_x$ catalyst. Reaction conditions: (a) $p(C_2H_6) = 45.5\,kPa$, $p(O_2) = 18.2\,kPa$, $m_{cat} = 0.2\,g$, $\tau = 0.036\,g\,s\,ml^{-1}$, $X(O_2) > 96\%$; (b) $p(C_3H_8) = 40\,kPa$, $p(O_2) = 20\,kPa$, $m_{cat} = 0.2\,g$, $\tau = 0.06\,g\,s\,ml^{-1}$, $X(O_2) > 95\%$.

temperature by preheating. In both cases, the alkane conversion increased on increasing temperature. Since the oxygen conversions amounted to 95–96% at the lowest temperature, an increase in alkane conversion with rising temperature was mostly due to thermal pyrolysis. An increase of ethylene yield was obtained in ODE without significant loss in selectivity. For ODP, neither yield nor selectivity was improved by increasing the reaction temperature. As reported earlier, the selectivity to propene in ODP is not significantly improved by varying the C_3H_8-to-O_2 ratio [1].

3.2. Comparison of autothermal operation for ODE on REO and Pt catalysts

As illustrated in Table 2, oxidative pyrolysis and catalytic oxidative dehydrogenation resulted in similar ethylene yields as those of thermal pyrolysis; the selectivities were, however, 20% lower for the oxidative dehydrogenation. The latter can be compensated by a small volume of the autothermal reactor. The ignition of the reaction is an important catalyst function. After ignition, reaction temperatures can be sustained at the desired level without significant external heat input. Although similar ethylene yields can be obtained in oxidative pyrolysis, the use of catalysts (noble metal, REO-based) allows the operation in an energy-efficient manner. The contact time for both types of catalyst are in the range of milliseconds; the advantage of REO is related to the high thermal stability of those materials. Thus, the effect of sintering which takes place when using supported Pt (e.g. in the form of a Pt-monolith at high temperatures) can be avoided in long-term operation. In general, autothermal operation using different catalysts looks promising for the production of ethylene from ethane.

3.3. Comparison of autothermal operation for ODP on REO and Pt catalysts

On REO-based catalysts, the maximum yield of propene was approximately 10% at conversions of

Table 2
Best ethylene yields and selectivities for different processes of ethane dehydrogenation

Reaction/catalyst	Temperature (°C)	$Y(C_2H_4)$ (%)	$S(C_2H_4)$ (%)
Thermal pyrolysis of ethane (commercial process)	780–920	42–48	80–84
Non-catalytic ODE (this work)	800	45–47	61–66
ODE on Pt-monolith (Ref. [4])	920–925	45–57	65–66
ODE on REO-based catalysts (this work)	855–867	34–46	66–68

approximately 50%; a yield of 17% was obtained at 77% of conversion. In this context, the recent study of Beretta et al. [3] using a Pt/yAl_2O_3 catalyst as well as the work of Huff and Schmidt [6] on the oxidative dehydrogenation of propane in autothermal conditions have to be considered. In both studies, the reported propene selectivities and yields did not exceed significantly the values obtained on REO-based catalysts. Although, a heterogeneous reaction pathway was proposed by Huff and Schmidt [6], Forzatti's group confirmed that a Pt catalyst serves primarily as an ignitor. Similar findings were reported for REO-based catalyst in our previous studies [1,2].

The best selectivity results from the present study, as well as from the literature, which were obtained at different degrees of propane conversion using autothermal operation are summarized in Fig. 2, where they are compared with results for the oxidative pyrolysis and non-oxidative catalytic dehydrogenation. Autothermal ODP in the presence of a catalyst (which implies catalytic ignition and subsequent gas-phase reactions) cannot be considered as a promising alternative to the existing technologies for the production of propene even when operating in an energy-efficient manner since the selectivities at the same level of conversion of 60% are lower than those in catalytic non-oxidative dehydrogenation. Catalytic autothermal operation can, however, be of interest when considering the cumulative selectivities to olefins. Non-catalytic oxidative pyrolysis gives better results regarding propene selectivities at conversions below 20% but suffers also from low propene selectivity with increasing conversion.

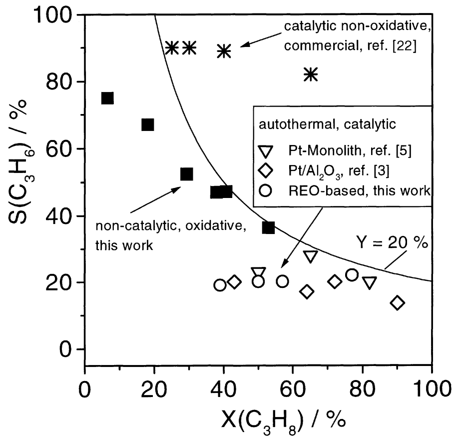

Fig. 2. Comparative results on propene selectivities at different degrees of conversions derived form the present study and from literature [3,5,22] for different operational modes of propane dehydrogenation.

3.3.1. Conclusion

There exists a crucial difference in the autothermal operation of ODP and ODE with respect to the formation of the olefins. The autothermal operation with both REO-based and Pt catalysts is very promising for the production of ethylene from ethane; yields of approximately 50% can be obtained. In ODP, however, not only propene but also ethylene is formed due to C–C bond scission and so the formation of propene occurs with low selectivities (<30%). Although cumulative yields of the two olefins as high as 50% can be obtained, the maximal yields of propene amounted to 17%. Thus, a search for new catalysts producing propene more selectively in the catalytic oxidative conversion of propane is still a challenging task.

3.4. Selection and optimization of catalytic materials using a combinatorial and evolutionary approach for ODP

An example of catalyst development using a combinatorial and evolutionary approach will now be given for redox-type mixed metal oxides. The selection of the primary redox compounds was based on the simplifying assumption that a medium O–Me binding energy is required to ascertain the participation of lattice oxygen in ODP. From those metal oxides having a free energy of oxide formation, $\Delta_f G$, per oxygen atom in the range between -400 and -200 kJ/mol, similar to that for V_2O_5 ($\Delta_f G = -311$ kJ/mol), the following compounds were selected as being expected to contribute to the ODP catalysis: V_2O_5, MoO_3, MnO_2, Fe_2O_3, ZnO, Ga_2O_3, GeO_2, Nb_2O_5, WO_3, Co_3O_4, CdO, In_2O_3, NiO.

The stoichiometric compositions of the catalytic materials prepared can be described as follows:

$$ {}^{1}\mathbf{A}_{\mathbf{x}_1}-{}^{2}\mathbf{A}_{\mathbf{x}_2}-{}^{3}\mathbf{A}_{\mathbf{x}_3}-\ldots-{}^{n-1}\mathbf{A}_{\mathbf{x}_{n-1}}-{}^{n}\mathbf{A}_{\mathbf{x}_n}-\mathbf{O}_{\mathbf{y}} \qquad (1) $$

where ${}^{i}\mathbf{A}$ is one of the following elements: V, Mo, Mn, Fe, Zn, Ga, Ge, Nb, W, Co, Ni, Cd, In and $\mathbf{x}_i$ is the atomic proportion of element ${}^{i}\mathbf{A}$ (stoichiometry).

The procedure applied in the present study implied

1. stochastic creation of a library of catalytic materials of the first generation based on the pool of primary components (according to Eq. (1));
2. preparation and testing of catalytic materials of the first generation;
3. selection of a certain proportion of those materials from the first generation which resulted in the best performance;
4. creation of a new library (second generation) based on the selected materials of the first generation using mutation and cross-over methods;
5. preparation and testing the second generation of catalytic materials;
6. repetition of (3)–(5) for the next generations.

As an arbitrary precondition, the different materials of the first generation (cf. Table 3) consisted of only three primary components and the total number of combinations of the first generation amounted to 20. In the subsequent generations, only 10 new compositions were applied; seven had been generated by mutation and three by cross-over [13].

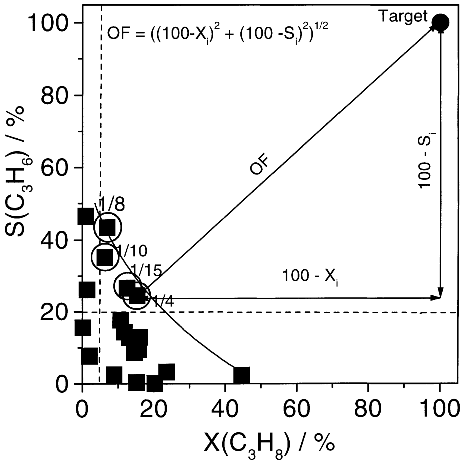

Fig. 3. Selectivity of propene as a function of propane conversion for the first generation of catalytic materials (T = 500°C, $C_3H_8/O_2/N_2 = 2/1/2$). Objective function as criterion of catalyst quality to be minimized in the next generations.

The catalytic materials were synthesized according to the method described in Section 2 and were then tested for their catalytic performances. The catalytic results of the first generation of materials are shown in Fig. 3 in which the dependence of propene selectivities on propane conversions is plotted. Besides

Table 3
Compositions of catalytic materials of the first generation

No.	Content												
	V	Mo	Mn	Fe	Zn	Ga	Ge	Nb	W	Co	Ni	Cd	In
1				0.79		0.02		0.19					
2		0.44									0.23		0.33
3					0.7		0.08			0.22			
4	0.33			0.43								0.24	
5						0.009		0.33			0.66		
6		0.33			0.42								0.25
7							0.11		0.33			0.56	
8	0.26		0.33			0.41							
9								0.16		0.33			0.5
10		0.42		0.53			0.44						
11	0.47								0.19		0.33		
12			0.41			0.51		0.08					
13		0.45								0.22			0.33
14				0.75			0.05		0.2				
15	0.33		0.43								0.23		
16					0.67			0.1		0.23			
17		0.33		0.42								0.25	
18						0.065			0.33		0.6		
19			0.33		0.41								0.25
20							0.14			0.33		0.53	

propene, CO and CO_2 were the main products; ethylene, methane, oxygenates (mainly acrolein) and C_4 hydrocarbons were also observed in minor amounts for some materials. A criterion of catalytic performance of the materials was defined, i.e. the objective function, OF (see Fig. 3); OF has to be minimized and is a measure of how close the results are to a yield of 100%. The selection of materials was furthermore restricted to those which resulted in conversions $\geq$5% and selectivities $\geq$20% (see the broken lines in Fig. 3).

The second generation of catalytic materials was produced based on the best materials of the first generation by applying a special software code implying the evolutionary operators (mutation, cross-over); a general description of the mutation and cross-over procedures is given in Ref. [13]. Hereby, changes in the stoichiometry of the best samples and variations of the qualitative chemical composition were accomplished. Four generations were prepared and tested for their catalytic performances. As a result of the optimization procedure, an increase in the propene yield was achieved with increasing number of generations. The propene yields obtained with the four best samples of each generation are shown in Fig. 4.

The use of an evolutionary approach resulted in an improvement of the catalytic performance. The highest C_3H_6 yield in the first generation amounted to 3.7% ($S = 24\%$) on $V_{0.33}Fe_{0.43}Cd_{0.24}O_x$ but in the fourth generation, an increase of the yield to 8.0% ($S = 36\%$) was achieved on $V_{0.19}Mn_{0.24}Fe_{0.32}Ga_{0.25}O_x$. This improvement involved not only an increased degree of conversion but also an increased selectivity. Thus, an improvement of catalyst quality was achieved although only a limited numbers of compositions were screened. Within the evolutionary procedure applied in this study, the number of primary components in

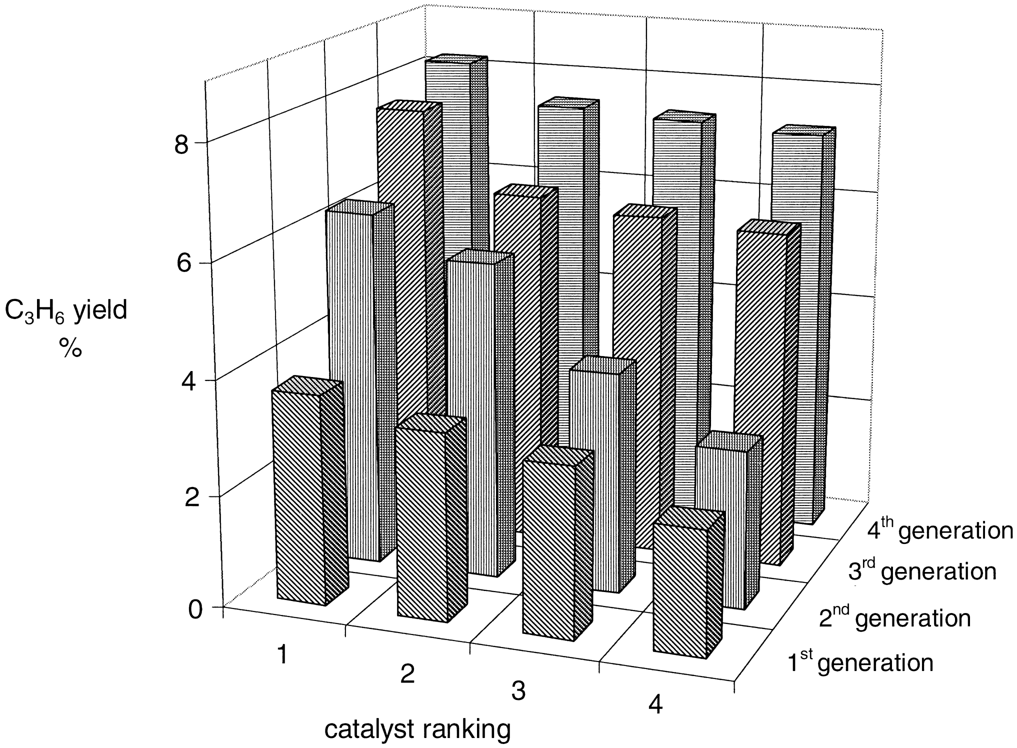

Fig. 4. Best propene yields achieved in each generation on the following catalytic materials (in the order of decreasing catalyst quality): first generation: $V_{0.33}Fe_{0.43}Cd_{0.24}O_x$, $V_{0.33}Mn_{0.43}Ni_{0.23}O_x$, $V_{0.26}Mn_{0.33}Ga_{0.41}O_x$, $Mo_{0.42}Ge_{0.44}Fe_{0.53}O_x$; second generation: $V_{0.47}Mn_{0.22}Ga_{0.31}O_x$, $V_{0.43}Mn_{0.54}Fe_{0.03}O_x$, $V_{0.26}Mo_{0.33}Fe_{0.41}O_x$, $V_{0.30}Fe_{0.48}Cd_{0.22}O_x$, third generation: $V_{0.2}Mn_{0.17}Fe_{0.32}Ga_{0.32}O_x$, $V_{0.47}Mn_{0.13}Ga_{0.38}O_x$, $V_{0.26}Mn_{0.33}Ga_{0.41}O_x$, $V_{0.37}Mn_{0.22}Fe_{0.41}O_x$, fourth generation: $V_{0.19}Mn_{0.24}Fe_{0.32}Ga_{0.25}O_x$, $V_{0.06}Mn_{0.02}Ga_{0.92}O_x$, $V_{0.49}Mn_{0.13}Ga_{0.38}O_x$, $V_{0.47}Fe_{0.19}Ga_{0.33}O_x$.

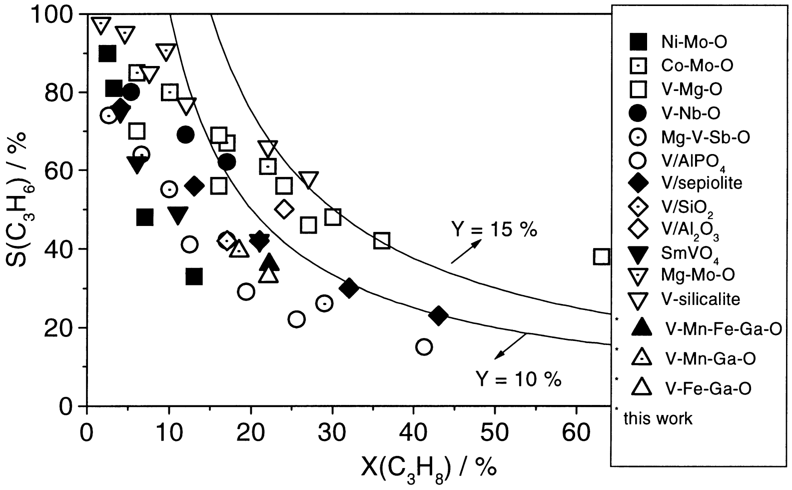

Fig. 5. Selectivities towards propene vs. propane conversion for different catalysts. For literature data see Ref. [23–33].

the catalytic materials decreased from the original 13 elements (see above) to only four (V, Mn, Fe, Ga). In general, such rapid narrowing of the pool of primary compounds should be avoided; this subject is presently being addressed [13].

The results obtained on three catalysts of the fourth generation (V–Mn–Fe–Ga–O, V–Mn–Ga–O, and V–Fe–Ga–O) are shown in Fig. 5 along with the best results on catalysts consisting of reducible oxides as reported in the literature [23–33].

4. Conclusions

ODE in an autothermal mode of operation may become a viable process. Ethylene yields are in the range of present technology applying non-oxidative thermal dehydrogenation. Small reactor volumes due to very short contact times in the millisecond range and operation in an energy-efficient manner are the advantages of such autothermal operation. Contrary to ODE, in which true dehydrogenation definitely prevails, C–C bond scission takes place in the autothermal operation of ODP leading to the formation of ethylene and methane in significant amounts in addition to the CO_x formed by total oxidation. Thus, the autothermal ODP process suffers from low propene selectivities and yields and needs innovative concepts in the development of catalysts. Against the latter requirement, some preliminary results on the use of the combinatorial and evolutionary approach have been reported. The evolutionary approach possesses significant potential in the identification of improved catalytic materials for a specific reaction from a broad basis of single compounds. Although there was an improvement of the catalyst quality obtained by the evolutionary optimization procedure, the results are not final since more generations of increased size have to be tested. Moreover, the present selection and optimization work was restricted to redox-type primary components; further improvements are expected when using other primary components. The inclusion of various preparation methods in the evolutionary process and the use of an appropriate software for data procurement will be further steps in our research.

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