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Solid 'oxygen reservoirs' for selective hydrogen oxidation

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Chapter 1

Introduction



This work has been submitted to a peer-reviewed journal.

1.1 General introduction

Cerium was discovered in 1803, by both Jöns Jakob Berzelius and Wilhelm Hisinger in Sweden, and Martin Heinrich Klaproth in Germany.^[1] It was named after the dwarf planet *Ceres*, discovered in 1801, which was in turn named after the Roman goddess of agriculture (particularly the growth of cereals).^[2] Cerium is part of the ceric or light rare-earth elements, and is the main component of the Bastnasite (USA, China), Monazite (Australia) and Loparite (Russia) rare-earth minerals.^[3] Cerium or cerium-oxide ('ceria') is used in various applications, such as the removal of free oxygen and sulphur from the melt in the casting of iron, as a polishing agent for glass and for the decolourisation of glass.^[3, 4] Due to their good ionic conduction, ceria-based materials can also be applied as electrolytes in solid oxide fuel cells.^[5] One of the most successful industrial applications of ceria is as oxygen storage material in automotive three way (catalytic) converters (TWC).^[6-9] Plain ceria has been used from the eighties onwards, and, in 2003, TWC sales accounted for one quarter of the global catalytic market.^[10] The successful application of ceria in TWCs is due to its temperature stability and its facile $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + e^-$ redox reaction, allowing the ceria to easily store and release oxygen.^[11] In the catalytic converter, this aids the hydrocarbon combustion in the fuel-rich mode, and the NO reduction in the fuel-lean mode. The application of ceria-based materials in TWCs has been reviewed by several authors.^[7, 10, 12] An excellent review on the physical and (electro-) chemical properties of ceria-based oxides was published by Mogensen *et al.* in 2001.^[13] The group of Trovarelli has performed a lot of work on the (redox) chemistry and catalysis of ceria and ceria-based materials,^[11, 14, 15] and a book on the subject was published in 2002.^[3]

The TWC is related to combustion engines running on conventional fuel, with the ceria aiding full combustion and NO reduction. In the last ten years, however, the research focus has shifted to alternative power sources, such as fuel cells, and alternative fuels, such as hydrogen. Furthermore, alternatives for crude oil for the production of (fine) chemicals are sought, such as the production of syngas from (bio-)methane, and the conversion of these to larger molecules by the Fischer-Tropsch process. Interestingly, in this field ceria-based materials have also gained a lot of attention, but contrary to the TWC, most recent literature focuses on selective oxidation applications rather than on full combustion. Many of these

recent papers deal with selective oxidation of CO from CO/hydrogen (preferential oxidation, PROX), often using copper-ceria, to clean up the hydrogen used in fuel cells.^[16-18] The CO removal is needed since it poisons the Pt-catalyst at the low operating temperatures used. Secondly, in the search for alternative fuels and chemical building blocks, the generation of syngas by partial oxidation of methane (POM), or methane steam reforming has gained a lot of attention.^[19-22] Ceria-based materials have also been used for selective oxidations of small molecules such as H₂S to S or H₂ to H₂O₂, and for selective oxidations of various hydrocarbons.^[23-28] In view of the topic of this thesis, I will discuss the performance of ceria-based materials in one type of selective oxidation, namely oxidative dehydrogenation (ODH). This yields valuable small alkenes such as ethene and propene. These can be used either as building blocks for various chemicals or high purity monomers for plastics such as polypropene and polyethene.

Ceria-based materials come in many forms. Ceria can act as support for 'active metals', but at low concentrations these metals can also be doped in the ceria's fluorite lattice, forming 'solid solutions'. Ceria can also form 'mixed oxides' with other metal oxides, drastically changing its catalytic properties. Importantly, the ceria's facile redox cycle often results in a strong metal-support interaction (SMSI), which can have a pronounced effect on the catalysis. I therefore start by explaining this interaction, as well as outlining some basic properties relevant to catalysis, before discussing ceria's role in ODH.

1.2 What are we dealing with? Some properties and pitfalls

There are various routes for synthesising ceria,^[3] but the simplest is by calcining ceriumnitrate, Ce(NO₃)₃.^[29, 30] At about 65 °C the ceriumnitrate melts, followed by dehydration and, from about 200 °C onwards, nitrate decomposition.^[31, 32] No further weight loss occurs above 400 °C, and this temperature is sufficient to form the ceria fluorite structure.^[32] At these low calcination temperatures, the ceria's crystallite size is small, and the surface area high. Ceria catalysts are often used at higher temperatures, however, and increasing the calcination temperature will increase the crystallite size, decreasing the specific surface area. Typical values obtained when preparing ceria by calcining ceriumnitrate are a crystallite size of 10 nm and surface area of 85 m²/g when

calcining at 550 °C, and a crystallite size of 25 nm and surface area of 30-50 m²/g when calcining at 700 °C.^[30, 33] High surface area cerias can be obtained by applying sol-gel or surfactant assisted synthesis methods.^[34-36] With these techniques, surface areas ranging from about 125 - 230 m²/g can be achieved, at calcination temperatures of 800 °C and 450 °C, respectively. The sintering behaviour of ceria is dependent on the gas atmosphere. Practically, this means that when a ceria catalyst is used in a reducing atmosphere, it can still sinter, even at temperatures below its calcination temperature. The sintering behaviour of ceria under various atmospheres is shown in Figure 1. All data was obtained starting from the same batch of ceria.^[37]

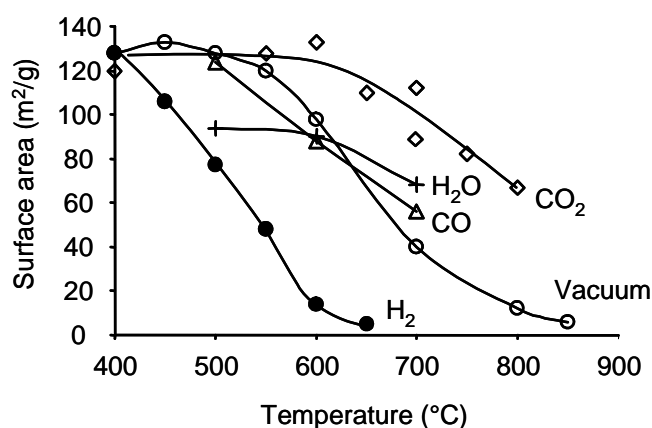
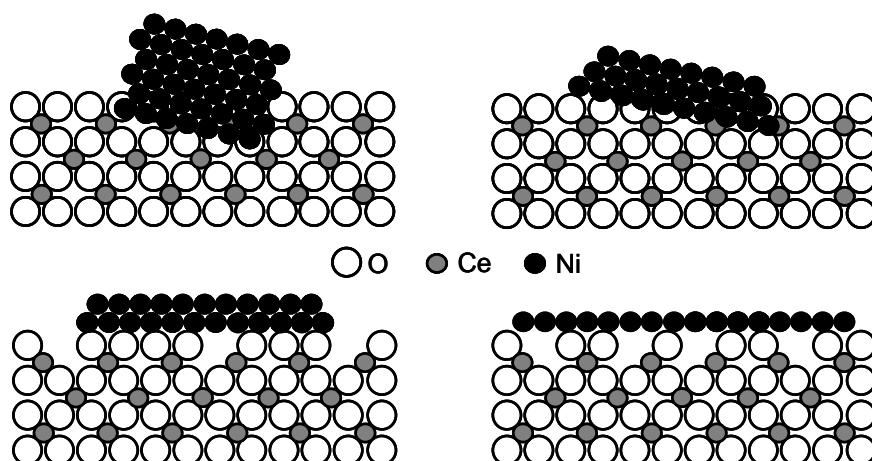


Figure 1. The specific surface area of plain ceria when heated in various gasses (at atmospheric pressure) and under vacuum.^[37] All data is obtained starting from the same batch of ceria. Data of the treatment in air is not added for clarity, but their trend is similar to those obtained in vacuum. Reproduced with permission of the author and the publisher.

The high temperatures encountered in automotive catalysis, typically 1000-1100 °C, sparked the search for ceria-based materials with a higher temperature stability. Ceria-zirconia mixed oxides have higher thermal stability and excellent redox behaviour.^[10, 33, 38-40] Indeed, ceria-based materials are versatile since the ceria can be used not only as support for active metals, but these metals can also be doped into the ceria lattice itself, or form ceria containing mixed oxides. Incorporation of dopant atoms in the ceria bulk allows for tuning the oxygen

conduction, the electronic conduction, and with them the catalytic properties.^[13, 41, 42] Importantly, the distinction between an active metal supported on ceria or doped into the ceria lattice is not always clear, especially at elevated temperatures and/or in the presence of reducing gasses. The facile redox of the ceria can result in strong metal-support interaction when ceria is used as support.^[43-45] Phase segregation or a change in phase composition can occur for ceria-based solid solutions and mixed oxides.^[39, 46] Thus, the active site can change during catalysis. For example, when nickel supported on ceria is reduced at 750 °C, the nickel crystallites can spread over the reduced ceria support (see Scheme 1).^[43] Conversely, at too high doping levels or temperatures, a dopant can segregate from the ceria as a separate oxide, or the catalyst's surface can be enriched in dopant atoms.^[47-50] Importantly, the spreading of nickel crystallites over the ceria surface in case of a ceria support, and the surface enrichment in case of the doped ceria could lead to similar surface structures. These effects also complicate catalyst characterisation. In case of XRD, for example, the absence of dopant oxide crystals does not prove dopant incorporation in the bulk. Indeed, several groups observed that when impregnating copper on ceria supports, no copper oxide phases were detected, provided that copper loading and calcination temperatures were kept low.^[51] Lattice doping can be demonstrated by using XRD, EXAFS or EPR.^[48, 52-55] This does not exclude, however, that the surface of the material, where catalysis takes place, is enriched with the dopant. A small amount of dopant or dopant oxide clusters, or a dopant enriched surface phase will not be detected by bulk techniques. Surface sensitive techniques such as LEIS and XPS can detect surface enrichment, and in case of XPS, the oxidation states of surface components.^[49] Their signal however, is still the average of the entire catalyst surface, which can complicate things if multiple types of surface species are present.



Scheme 1. Proposed spreading of nickel supported on ceria upon reduction to 750 °C, drawn after Gonzalez-DelaCruz.^[43]

Another type of strong metal-support interaction is the so-called ‘decoration’ of Pd, Pt and Rh by ceria observed upon reduction to 600-700 °C. Contrary to nickel, the supported metal crystals stay intact, but are decorated with a layer of ceria upon the high-temperature reduction, shielding the noble metal's surface and thereby affecting the catalysis (see Figure 2).^[44] Note that this shielding effect can not be observed by, for example, XRD.

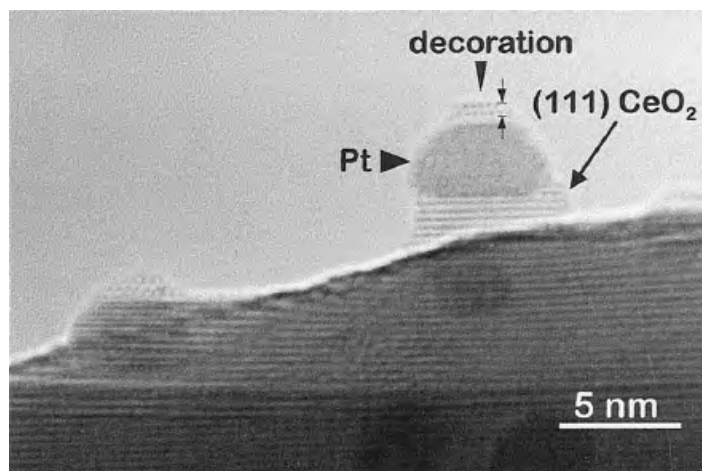
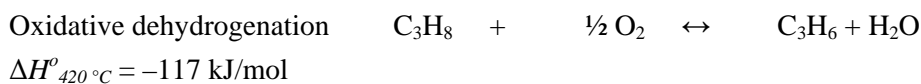
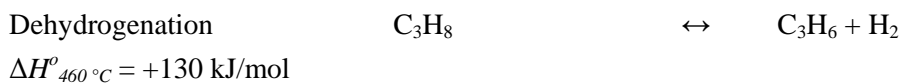


Figure 2. Metal decoration of 4 wt% Pt supported on ceria upon reduction in hydrogen at 700 °C.^[44] Reproduced with permission of the author and the publisher.

1.3 Oxidative dehydrogenation (ODH) using ceria-based materials

The demand for small alkenes is high. Propene demand, for example, is expected to rise to 80 million tonnes in 2010 worldwide.^[56-58] The main routes to propene are steam cracking, fluid catalytic cracking, and catalytic dehydrogenation. All these processes are endothermic. Advantageous on-demand production of alkenes is achieved by catalytic dehydrogenation, but it is equilibrium limited and deactivation of the catalyst occurs due to coking (the formation of a carbon-rich solid on the catalyst's surface).^[59-61] Oxidative dehydrogenation (ODH), where oxygen or an oxygen containing molecule such as N₂O or CO₂ is added to the gas feed, can overcome these limitations, allowing exothermic, non equilibrium-limited, and on-demand production of the alkenes (see Scheme 2).^[61] Furthermore, the addition of oxygen limits catalyst deactivation due to coking. It can, however, result in over-oxidation of the hydrocarbons to CO and CO₂.^[62] This is a big challenge, since the alkene product is more reactive than the alkane starting material. Thus, specific ODH catalysts have to be developed, and up till now, (supported) vanadium or molybdenum oxides have gained most attention.^[61] For ethane ODH, yields comparable to those of steam cracking are obtained, but propane ODH yields are still far from being interesting for industry. In both cases, little is reported on catalyst lifetime.^[61] In the search for better ODH catalysts,

various ceria-based materials have also been investigated. The results are summarised in the following sections.



Scheme 2. Propane dehydrogenation (top)^[63] and oxidative propane dehydrogenation (bottom)^[64]

1.3.1 Oxidative dehydrogenation of ethane

Table 1 gives the catalyst composition and catalytic performance of ceria-based materials as catalysts for ethane ODH (note that some data is taken from figures, not tables). Doped ceria's (or solid solutions, where the crystal structure of the ceria remains unchanged by the addition of the dopant), or mixed oxides containing metal M and ceria are denoted as 'Ce-M-O'. Metal M supported on ceria is denoted as 'M/CeO₂'. The catalysts generally give a high selectivity towards ethene at low conversion, and lower selectivities at high conversion. I have therefore incorporated the data of the highest selectivity, highest activity, and highest overall performance in the table, where available. The activity and selectivity data in the table is presented graphically in Figure 3.

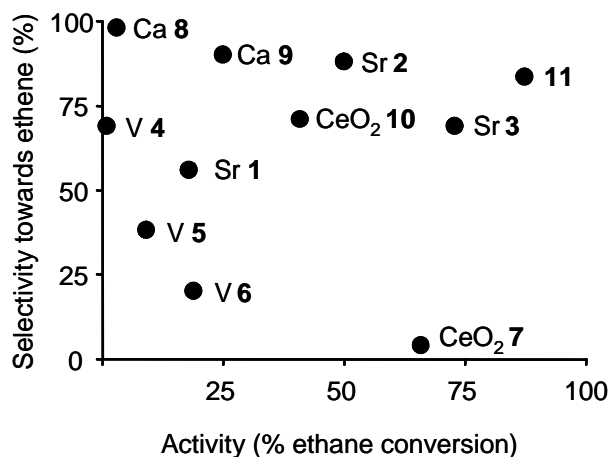


Figure 3. Activity and selectivity in ethane ODH. The labels show the type of metal added to the ceria, and the catalyst number. A Mo-V-Te-Nb-mixed oxide catalysts (**11**) is added for reference.

The data show that the best catalysts, achieving highest selectivity and activity, are the calcium doped **9**, the supported strontium **2** and **3** and the plain ceria **10**. Interestingly, most of these catalysts were tested under special conditions: steam was added in case of **2**, increasing the activity by dilution and the selectivity by prevention of coking, and the ODH was performed with CO₂ instead of oxygen in case of **9** and **10**.^[65-67] The ODH with CO₂ was performed at rather high temperatures (≥ 750 °C), which is higher than the temperature needed for the (endothermic) catalytic dehydrogenation.^[68] The vanadium-containing catalysts **4–6** run below 600 °C, but also with lower activity and selectivity. The supported Sr **3** has rather high selectivity and activity at 660 °C, running without addition of steam, nor using CO₂ as the oxidant.^[69] Their performance falls short, however, compared to the best reference catalyst **11**, a V and Mo containing mixed oxide, which also operates at lower temperature (400 °C) and without steam and/or CO₂. (see Table 1 and Figure 3). Note however, that catalyst **11** is one of three catalysts, out of 70 tested, which displays this good performance,^[61] and that the other 67 catalysts have substantially lower activity and selectivity. Far less research has been performed on ceria-based materials. No data is available, for example, for molybdenum-containing ceria-based materials, although the data on Ce-V-O shows

that using components of the benchmark reference catalysts does not guarantee good performance in ceria-based materials (*vide infra*). Indeed, in a pre-screening for a combinatorial catalysis approach, Ni-Ce-Nb and Ni-Ce-Ta mixed oxides were found to be the most interesting leads, outperforming the best Mo-V-Nb oxide in ethane ODH.^[70] Up till now, no Ce-Ni-O or Ce-(Ni, Nb, Ta)-O catalyst was tested for the ethane ODH.

Interestingly, *operando* studies with vanadia supported on ceria show that this system is highly interactive, as was seen for nickel and noble metals supported on ceria.^[71-73] Starting from vanadia supported on ceria, the vanadia interacts strongly with the ceria, eventually forming a CeVO₄ phase. Surprisingly, this process does not affect the selectivity and activation energy in the ethane ODH.^[73] Possibly, the active phase consists of Ce³⁺-O-V⁵⁺, which is present in both supported vanadia and the CeVO₄. This also explains why the catalytic properties of Ce-V-O materials differ from other vanadium containing ODH catalysts (which are the ODH benchmark).

Table 1. Ceria-based materials used for ethane ODH.

Catalyst number	Catalyst comp.	Concentration added metal	Alkane:O ₂ ^[a]	Space velocity (ml/g.h) ^[b]	Temperature (°C)	Ethane conversion (%)	Selectivity towards ethene (%)	Reference
1	Sr/CeO ₂	10 mol%	6:1 (molar)	10200	700	18	56 ^[c]	[74]
2					800	50	88 ^[c]	
3	SrCl ₂ /CeO ₂	30 mol%	2:1	6000	660	73	69	[75]
4	V/CeO ₂	3 wt%	1:2	90000	510	1	69	[71-73]
5		3 wt%			590	9	38	
6		1 wt%			590	19	20	
7	CeO ₂ ref.				550 ^[d]	66	4	
<i>Using CO₂ instead of oxygen:</i>								
8	Ce-Ca-O	10 mol%	1:2 (CO ₂)	12000	650	3	98 ^[e]	[68]
9					750	25	90	
10	CeO ₂ ref.				750	41	71	
<i>Non-ceria-based reference catalyst:</i>								
11	Mo-V-Te-Nb	1:0.2:0.17:0.17	9:6	100	400	87	84	[76]

^[a] CO₂ when applicable. ^[b] Reactions were performed at atmospheric pressure. ^[c] Steam was added at H₂O:C₂H₆ = 1:1 molar ratio.

^[d] Same performance at 510 and 590 °C. ^[e] This is the value obtained after pre-treating the catalyst at 750 °C under the reaction conditions. The fresh catalyst has a selectivity of ~55%, and the increase in selectivity is irreversible.

1.3.2 Oxidative dehydrogenation of propane

The success of nickel-containing catalysts in propane and isobutane ODH, has led to the testing of nickel-containing ceria-based catalysts in propane ODH.^[77, 78] The group of Barboux showed that using nickel-containing ceria-based catalysts, ODH can be performed at lower temperatures, as compared to when the other nickel catalysts are used (300 °C).^[77] Upon comparing ceria-nickel mixed oxides with nickel supported on ceria, it was found that the supported catalysts gave the highest selectivity, but low conversion (see Table 2, **1**). The mixed oxides give higher conversion, but lower selectivity (**2** and **3**, all data taken at 300 °C). Nickel-containing mixed oxides were found to be superior in yield as compared to mixed oxides with either Cr, Co, Cu or Zn (catalysts **4**, **5**, and **6**).^[79] Note that the mixed oxides from both studies, at the same composition and reaction temperature, differ strongly in activity and selectivity (compare **2** and **5**, note that both space velocity and conversion of **5** are higher). The preparation methods of the catalysts are very similar, except for the calcination temperature (700 °C for **2**, 500 °C for **5**). As was the case for ethane ODH, the supported vanadium catalysts perform less well than other ceria-based mixed oxides (catalysts **7-9**, Table 2).^[78]

Contrary to the ethane ODH experiments shown in Table 1, the propane ODH is performed at temperatures well below that of the catalytic propane dehydrogenation, albeit at rather low conversion. No data is available on the use of other oxidants, such as CO₂, but the selectivity of plain ceria is seen to increase substantially when adding trichloromethane gas (**10-12**).^[80] It is worthwhile to investigate the effect of halogen addition on the catalyst performance in propane ODH via a more practically applicable route, such as using supported metal-halogens, as was done for the ethane ODH.^[75] As was the case in ethane ODH, the non-ceria-based reference catalyst (**13**) outperforms the ceria-based ones. But again, much more non-ceria-based catalysts have been tested, and the large majority of these perform less well than **13**.

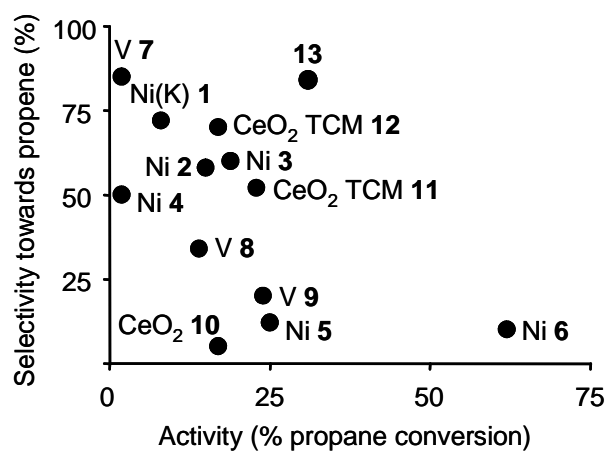


Figure 4. Activity and selectivity in propane ODH. The labels show the type of metal added to the ceria, and the catalyst number. A supported vanadia catalyst (**13**) is added for reference.

Table 2. Ceria-based materials used for propane ODH.

Catalyst number	Catalyst comp.	Concentration added metal	Alkane:O ₂	Alkane, O ₂ conc. (% v/v)	Space velocity (ml/g.h) ^[a]	Temperature (°C)	Propane conversion (%)	Selectivity towards propene (%)	Ref.
1	Ni-K/CeO ₂	Ni:Ce = 1, K:Ni = 0.05 ^[b]	1:2	4, 8	545	300	8	72	[77]
2	Ce-Ni-O	Ni:Ce = 0.5 ^[b]					15	58	
3	Ce-Ni-O	Ni:Ce = 1 ^[b]					19	60	
4	Ce-Ni-O ^[c,d]	Ni:Ce = 0.5 ^[b]	1:3	5, 15	30000	200	2	50	[79]
5						300	25	12	
6						375	62	10	
7	V/CeO ₂	12 wt%	1:3	5, 15	5000	300	2	85	[78]
8		6 wt%				300	14	34	
9		6 wt%				400	24	20	
10	CeO ₂		1:1	14, 13 ^[e]	3600	450	17	5	[80]
11	CeO ₂ +TCM	17% v/v TCM ^[f]	1:1	14, 13 ^[e]			23	52	
12	CeO ₂ +TCM	17% v/v TCM	3.5:1	14, 4 ^[e]			17	70 ^[g]	
<i>Non-ceria-based reference catalyst:</i>									
13	V/MCF ^[h]	4.2 wt %	1:1	10, 10	72000	550	31	84	[81]

^[a] Reactions were performed at atmospheric pressure. ^[b] These are atomic ratios. ^[c] Reference measurements were performed on ceria and nickel oxide. Ceria: 3% conversion, 2% selectivity (300 °C), 10% conversion, 6%, selectivity (400 °C, note: quite close to entry **10**). NiO 10% conversion, 17%, selectivity (350 °C). ^[d] Ni outperforms similar catalysts containing Cr, Co, Cu or Zn. ^[e] The concentration is in kPa instead of %v/v. ^[f] TCM stands for trichloromethane. ^[g] At this oxygen pressure the values for plain ceria are: 7% conversion, 10% selectivity. ^[h] MCF stands for Miscellous Silica Foams.

1.3.3 Oxidative dehydrogenation of other hydrocarbons

Besides ethane and propane, ceria-based materials have been applied in isobutane and ethylbenzene ODH (see Table 3). High selectivity and conversion, at temperatures lower than those at which commercial catalysts are used, were obtained for ethylbenzene ODH over plain ceria, using N_2O as oxidant (1).^[82] The high activity was attributed to a high concentration of $Ce^{4+}-O^- - Ce^{3+}$ defect sites. Both doped and supported chromium-ceria catalysts were applied in the isobutane ODH (see Figure 5).^[83, 84] The chromium containing catalysts show better results than plain ceria. The activity of chromium supported on ceria is higher than plain chromium oxide and the chromium ceria mixed oxide (this is the case at both 270 °C and 300 °C). Conversely, the selectivity of the chromium supported on ceria is somewhat lower as compared to the ceria chromium mixed oxides and plain Cr_2O_3 . In case of the chromium-ceria systems, well dispersed $Cr^{6+}-O_x$, and not Cr_2O_3 aggregates, was proposed as the active site, which was poisoned by the presence of potassium.^[84]

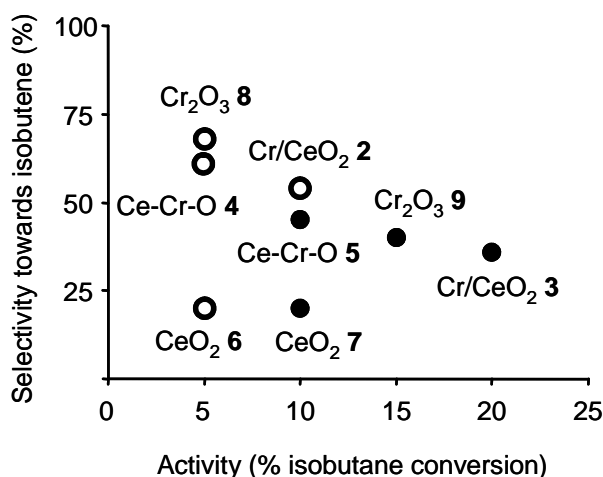


Figure 5. Isobutane ODH over chromium-ceria catalysts at 270 °C (open circles) and 300 °C (full circles). The labels show the type of metal added to the ceria, and the catalyst number. Plain ceria and Cr_2O_3 are added for reference.

Table 3. Ceria-based materials used for ethylbenzene and isobutane ODH.

Catalyst number	Catalyst comp.	Concentration added metal	Reactant	Space velocity (ml/g.h)	Temperature (°C)	Alkane conversion (%)	Selectivity towards alkene (%)	Ref.
1	CeO ₂		Ethylbenzene ^[a]	-	325	45	94	[82]
2	Cr/CeO ₂	5-40 Cr atoms / nm ²	Isobutane ^[b]	-	270	10	54	[83]
3					300	20	36	
4	Ce-Cr-O	Cr:Ce = 0.2-1.8 ^[c]			270	5	60	
5		Cr:Ce = 0.2-1.8 ^[c]			300	10	45	
6	CeO ₂				270	5	20	
7					300	10	20	
8	Cr ₂ O ₃				270	5	68	
9					300	15	40	

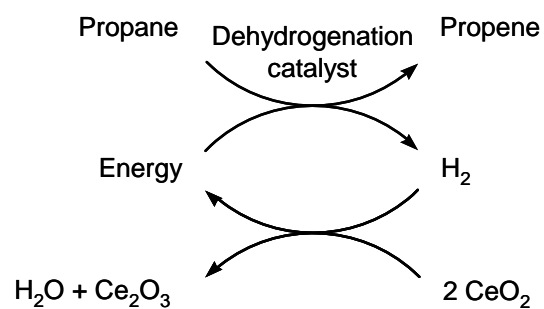
^[a] N₂O was used instead of O₂. No data on the reactant concentrations is given. ^[b] The isobutane : O₂ ratio is 1 : 1, at 6.5% v/v.

^[c] These are (bulk) atomic ratios.

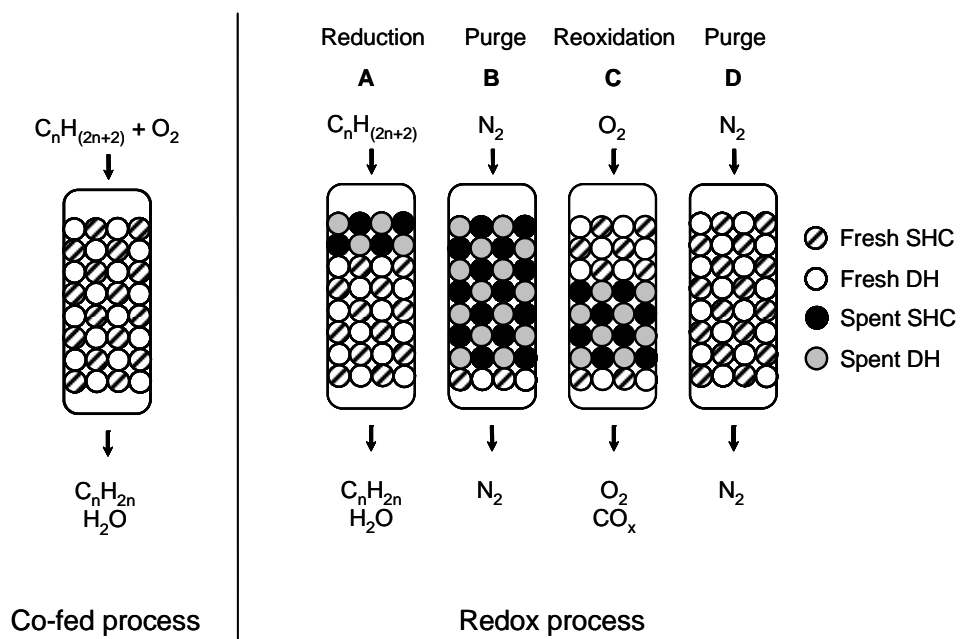
1.3.4 Combined dehydrogenation and selective hydrogen combustion

Another type of ODH has been industrially implemented. Here, the dehydrogenation is performed over a conventional dehydrogenation catalyst, and a second catalyst is added to selectively combust part of the hydrogen formed. The process may be therefore viewed as ‘two-step ODH’ (Scheme 3). The selective hydrogen combustion generates heat and shifts the equilibrium to the products side, yielding the same benefits as the ‘conventional’ ODH. The use of two catalysts or two reactors, however, allows for separate tuning of the dehydrogenation and the hydrogen oxidation reactions, and the advantage of this over conventional ODH is proven by the industrial implementation of the process. For example, the STAR (Steam Active Reforming) oxydehydrogenation process is implemented in two plants for the ODH of isobutane to MTBE. In this process, an oxydehydrogenation reactor is placed after a STAR-dehydrogenation reactor, both using the same catalyst.^[85] The SMART process (Styrene Monomer Advanced Reheat Technology) is in operation in five plants for the ODH of ethylbenzene to styrene. This process uses two catalysts in one reactor (the selective hydrogen combustion catalyst is Pt-based).^[86, 87] In both processes, steam is added to minimise coking and dilute the feed. These processes use a *co-fed* approach, where small amounts of oxygen are added to the gas feed (Scheme 4, left). The mixing of gaseous oxygen with hydrogen and hydrocarbons at elevated temperatures is, however, a safety risk, which is avoided in the *redox-mode* (Scheme 4, right). Here, no gaseous oxygen is added, but the lattice oxygen of the selective hydrogen combustion catalyst is used. At one point in time, however, the lattice oxygen is depleted and has to be refilled. That is, the reactor has to be purged and an oxygen containing feed has to be applied to the catalyst bed, resulting in a cyclic process. Note that the conventional DH catalyst also has to be regenerated periodically to burn off the coke accumulated on its surface. In redox mode ODH of ethane and propane, high selectivities towards hydrogen combustion can be obtained for several supported oxides (e.g. Sb_2O_4 , In_2O_3 , WO_3 , PbO and Bi_2O_3).^[88-91] These are, however, unstable under the high temperature redox cycling. The melting point of most of these metals lies below the operating temperature, and when the supported metal oxide is reduced to metal(0), it liquefies, causing sintering and deactivation. Conversely,

ceria is stable under the redox cycling conditions, and has a good oxygen storage capacity. The selectivity of plain ceria is low, but in a screening experiment, working with hydrogen/ethane/ethene mixtures, we showed that doping the ceria lattice can overcome both the problems of low selectivity and low stability.^[92] In this thesis, we investigated the fundamentals of this oxidative dehydrogenation process.



Scheme 3. Catalytic cycle for redox mode oxidative dehydrogenation using ceria as solid oxygen reservoir.



Scheme 4. Left: scheme of a co-fed mode oxidative dehydrogenation process. Right: scheme of a redox-mode dehydrogenation process (SHC: selective hydrogen combustion catalyst). After the dehydrogenation step **A**, the bed is flushed with nitrogen (**B**), and the catalysts are regenerated through reoxidation (**C**). This burns coke from the dehydrogenation catalyst and restores the lattice oxygen of the selective hydrogen combustion catalyst. After another nitrogen flush (**D**) the reactor is ready for the next redox cycle.

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