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Solid 'oxygen reservoirs' for selective hydrogen oxidation

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Appendix II: Catalyst activity

II.a Catalyst activity expressed in various units

II.b Catalyst activity in the mixed dehydrogenation and selective hydrogen combustion process

II.a Catalyst activity expressed in various units

The amounts of oxygen released by the SOR catalysts is determined via the reduction in hydrogen (TPR and TGA analysis), and by the amount of hydrogen combusted from the dehydrogenation gas mixture (4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 550 °C). This ‘oxygen storage capacity’ can be expressed in several ways, such as mass over mass, mass over volume and so on. In this section, the activity data, mainly from the catalysts of Chapter 3.1, is given in several units.

Tables A.1 and A.2 show the oxygen release of several SORs determined by H₂-TPR. Generally, the ‘mol O / kg catalyst’ allows for an easy comparison. The data of catalysts **1–7** is taken from Chapter 3.1. Catalyst **8** is plain ceria calcined at low temperature (550 °C instead of 700 °C), resulting in a larger surface area. The ‘**Ref.**’ data is the theoretical maximum amount of oxygen which can be released from ceria, when full (surface and bulk) reduction to Ce₂O₃ occurs. That is, a maximum 25% of the available oxygen can be released (note that we did not heat any sample above 800 °C).

Table AII.1 shows the oxygen release of the catalysts calculated from the size of TPR peak **C** (surface reduction, see Scheme 2 in Chapter 3.1). Catalysts **7** and **8** show that the amount of oxygen released (by weight or volume catalyst), nearly doubles when doubling the catalyst surface area. This shows that optimising the catalyst synthesis method is a promising route for increasing catalyst activity. Where our synthesis method yields surface areas of about 20–50 m²/g, alternative synthesis methods can give surface areas of 125–160 m²/g for ceria or ceria zirconia mixed oxides.^[1, 2] The highest surface area reported is 230 m²/g (when calcining at 450 °C).

Table AII.2 shows the ‘total’ oxygen release of the catalysts, calculated from both TPR peak **C** and peak **B** (surface and bulk reduction, see Scheme 2 in Chapter 3.1). Since bulk reduction occurs above 600 °C, this oxygen will not be available in the dehydrogenation reaction (generally performed at 550–600 °C).

Table AII.1. Quantitative TPR data part I: surface reduction (TPR peak C).^[a]

Catalyst/ Composition	Surface area (m ² /g)	Crystallite size (nm)	mg O / 100 mg sample ^[b]	Size TPR peak C (surface reduction) ^[a]			
				mg O / m ² surface area	kg O / m ³ sample ^[c]	mol O / kg sample	kmol O / m ³ sample ^[c]
1 Ce _{0.91} Mn _{0.09} O ₂	56	11	0.88	0.16	67	0.57	4.2
2 Ce _{0.90} Bi _{0.10} O ₂	33	18	1.24	0.38	95	0.80	5.9
3 Ce _{0.90} Cu _{0.10} O ₂	47	15	1.22	0.26	93	0.75	5.8
4 Ce _{0.90} Fe _{0.10} O ₂	50	14	1.15	0.23	88	0.75	5.5
5 Ce _{0.92} Pb _{0.08} O ₂	56	13	1.24	0.22	95	0.80	5.9
6 Ce _{0.91} Ca _{0.09} O ₂	22	28	0.47	0.22	36	0.29	2.2
7 CeO ₂	38	26	0.38	0.10	29	0.23	1.8
8 CeO ₂ 'C550' ^[d]	84	10	0.71	0.08	54	0.43	3.4
Ref. CeO ₂ → Ce ₂ O ₃ ^[e]	-	-	4.65	-	356	2.91	22.2

^[a] Peak A in case of catalyst **7** and **8** (ceria). ^[b] Data obtained by calibrating the TCD detector using a CuO standard. The peak area of this standard is integrated and the area is correlated to the amount of oxygen present in the CuO. ^[c] Note that the values per volume sample are given as 'kg' and 'kmol' instead of 'mg' and 'mol'. ^[d] This plain ceria sample was calcined at 550 °C instead of 700 °C (**1-7**), resulting in a higher surface area and smaller crystallite size. ^[e] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.2. Quantitative TPR data part II: surface and bulk reduction (TPR peak **C+B**).^[a]

Catalyst/ Composition	Surface area (m ² /g)	Crystallite size (nm)	Size TPR peak C+B (surface and bulk reduction) ^[a]				
			mg O / 100 mg sample ^[b]	mg O / m ² surface area	kg O / m ³ sample ^[c]	mol O / kg sample	kmol O / m ³ sample ^[c]
1 Ce _{0.91} Mn _{0.09} O ₂	56	11	1.18	0.21	90	0.77	5.6
2 Ce _{0.90} Bi _{0.10} O ₂	33	18	1.96	0.60	150	1.28	9.4
3 Ce _{0.90} Cu _{0.10} O ₂	47	15	1.68	0.36	129	1.04	8.0
4 Ce _{0.90} Fe _{0.10} O ₂	50	14	1.93	0.39	148	1.26	9.2
5 Ce _{0.92} Pb _{0.08} O ₂	56	13	1.56	0.28	119	1.01	7.5
6 Ce _{0.91} Ca _{0.09} O ₂	22	28	1.72	0.78	132	1.04	8.2
7 CeO ₂	38	26	1.21	0.32	93	0.75	5.8
8 CeO ₂ 'C550' ^[d]	84	10	1.03	0.12	79	0.63	4.9
Ref. CeO ₂ → Ce ₂ O ₃ ^[e]	-	-	4.65	-	356	2.91	22.2

^[a] Peak **A+B** in case of catalyst **7** and **8** (ceria). ^[b] Data obtained by calibrating the TCD detector using a CuO standard. The peak area of this standard is integrated and the area is correlated to the amount of oxygen present in the CuO. ^[c] Note that the values per volume sample are given as 'kg' and 'kmol' instead of 'mg' and 'mol'. ^[d] This plain ceria sample was calcined at 550 °C instead of 700 °C (**1-7**), resulting in a higher surface area and smaller crystallite size. ^[e] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.3 and AII.4 show the oxygen release of the catalysts when reduced in hydrogen at 550 °C in a TGA set-up (see Chapter 3.1). Table AII.3 shows the oxygen released during the fast part of the reduction curve (surface reduction), Table AII.4 shows the oxygen released in both the fast and slow part (see Scheme 2 in Chapter 3.1). Note that the experiment was stopped after 15 min. Reducing longer will increase the amount of oxygen released, but not to a great extent (see Figure 3 in Chapter 3.1).

Table AII.3. Quantitative TGA data part I: 'fast reduction' part (550 °C).

Catalyst/ Composition	Surface area (m ² /g)	Crystallite size (nm)	mg O / 100 mg sample	Size 'fast reduction' part			
				mg O / m ² surface area	kg O / m ³ sample ^[a]	mol O / kg sample	
1 Ce _{0.91} Mn _{0.09} O ₂	56	11	0.56	0.10	43	0.49	2.7
2 Ce _{0.90} Bi _{0.10} O ₂	33	18	1.23	0.37	94	0.92	5.9
3 Ce _{0.90} Cu _{0.10} O ₂	47	15	1.00	0.21	77	0.77	4.8
4 Ce _{0.90} Fe _{0.10} O ₂	50	14	1.30	0.06	99	0.83	6.2
5 Ce _{0.92} Pb _{0.08} O ₂	56	13	0.84	0.15	64	0.63	4.0
6 Ce _{0.91} Ca _{0.09} O ₂	22	28	0.30	0.03	23	0.23	1.4
7 CeO ₂	38	26	0.33	0.08	25	0.27	1.6
8 CeO ₂ 'C550' ^[b]	84	10	n.d. ^[c]	n.d.	n.d.	n.d.	n.d.
Ref. CeO ₂ → Ce ₂ O ₃ ^[d]	-	-	4.65	-	356	2.91	22.2

^[a] Note that the values per volume sample are given as 'kg' and 'kmol' instead of 'mg' and 'mol'. ^[b] This plain ceria sample was calcined at 550 °C instead of 700 °C (1–7), resulting in a higher surface area and smaller crystallite size. ^[c] Not determined. ^[d] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.4. Quantitative TGA data part II: Total oxygen release (15 min measurement, 550 °C).

Catalyst/ Composition	Surface area (m ² /g)	Crystallite size (nm)	Total oxygen release (15 min measurement)				
			mg O / 100 mg sample	mg O / m ² surface area	kg O / m ³ sample ^[a]	kmol O / m ³ sample ^[a]	
1 Ce _{0.91} Mn _{0.09} O ₂	56	11	0.78	0.14	60	0.49	3.7
2 Ce _{0.90} Bi _{0.10} O ₂	33	18	1.54	0.47	118	0.92	7.4
3 Ce _{0.90} Cu _{0.10} O ₂	47	15	1.22	0.26	93	0.77	5.8
4 Ce _{0.90} Fe _{0.10} O ₂	50	14	1.32	0.27	101	0.83	6.3
5 Ce _{0.92} Pb _{0.08} O ₂	56	13	1.07	0.19	82	0.63	5.1
6 Ce _{0.91} Ca _{0.09} O ₂	22	28	0.32	0.14	24	0.23	1.5
7 CeO ₂	38	26	0.43	0.10	33	0.27	2.0
8 CeO ₂ 'C550' ^[b]	84	10	n.d. ^[c]	n.d.	n.d.	n.d.	n.d.
Ref. CeO ₂ → Ce ₂ O ₃ ^[d]	-	-	4.65	-	356	2.91	22.2

^[a] Note that the values per volume sample are given as 'kg' and 'kmol' instead of 'mg' and 'mol'. ^[b] This plain ceria sample was calcined at 550 °C instead of 700 °C (**1–7**), resulting in a higher surface area and smaller crystallite size. ^[c] Not determined. ^[d] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.5 and AII.6 show the catalyst activity in the selective hydrogen combustion from a mixture with propane and propene. The reaction conditions are: 10 min cycles of 4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar (total flow 50 mL/min), with 5 mL/min of N₂ added as internal standard, 550 °C, 250 mg of catalyst (about 0.25 cm³), GHSV 13200 / h and WHSV 1.2 / h (calculated from the weight of C₃H₈ + C₃H₆ + H₂ per h per the weight of the catalyst). The activity is expressed in two ways, Table AII.5 shows the catalysts 'oxygen demand'. This is the total amount of oxygen used by the catalysts in the reoxidation step, to refill the ceria lattice and to combust the coke. It therefore represents both selective and unselective processes.

Table AII.5. Activity in the selective hydrogen combustion at 550 °C part I: oxygen demand.^[a]

Catalyst/ Composition	Surface area (m ² /g)	Crystallite size (nm)	mg O / 100 mg sample	Oxygen demand		
				mg O / m ² surface area	kg O / m ³ sample ^[b]	kmol O / m ³ sample ^[b]
1 Ce _{0.91} Mn _{0.09} O ₂	56	11	1.90	0.34	145	1.19
2 Ce _{0.90} Bi _{0.10} O ₂	33	18	1.70	0.52	130	1.06
3 Ce _{0.90} Cu _{0.10} O ₂	47	15	1.40	0.30	107	0.88
4 Ce _{0.90} Fe _{0.10} O ₂	50	14	3.00	0.60	230	1.88
5 Ce _{0.92} Pb _{0.08} O ₂	56	13	1.10	0.20	84	0.69
6 Ce _{0.91} Ca _{0.09} O ₂	22	28	0.20	0.09	15	0.13
7 CeO ₂	38	26	0.60	0.16	46	0.38
8 CeO ₂ 'C550' ^[c]	84	10	0.40	0.05	31	0.25
Ref. CeO ₂ → Ce ₂ O ₃ ^[d]	-	-	4.65	-	356	2.91

^[a] Conditions: 10 min cycles of 4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 50 mL/min total flow, 550 °C, 250 mg of catalyst (about 0.25 cm³), GHSV 12000 /h. The oxygen demand is the oxygen consumed by the catalyst during reoxidation, both to refill the lattice oxygen and to combust the coke. ^[b] Note that the values per volume sample are given as 'kg' and 'kmol' instead of 'mg' and 'mol'. ^[c] This plain ceria sample was calcined at 550 °C instead of 700 °C (1-7), resulting in a higher surface area and smaller crystallite size. ^[d] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.6 shows the ‘hydrogen activity’ of the catalysts. This is the amount of the hydrogen feed which is combusted by the catalysts, and therefore represents the selective reaction only. Besides catalysts **1–8** and the **Ref.** data, the data of the most active doped cerias (**9–12**), the most active perovskites (**13, 14**, and **15**), and the most active and selective material discovered up to date, PbCrO_4 (**16**), are given. Note that the surface areas of the perovskites and the PbCrO_4 are very low (0–6 m^2/g), leaving room for improvement. Interestingly, the ‘real’ activity of PbCrO_4 (**16**), i.e. the hydrogen combustion in simulated reaction conditions (in the presence of the hydrocarbons and at 550 °C), is comparable to the theoretical maximum activity of the doped cerias (**Ref.**, 2.8 mol O /kg and 2.9 mol O / kg, respectively). Note that we have only done preliminary tests using pure PbCrO_4 powder, which activity drops to about 25% of the initial value during prolonged redox cycling (125 cycles, 73 h on stream, see Chapter 2.3). This catalyst has yet to be optimised concerning stability.

Table AII.6. Activity in the selective hydrogen combustion at 550 °C part II: Hydrogen activity.^[a]

Catalyst/ Composition	Surface area			% H ₂ combusted ^[c]	Hydrogen activity			mol O / kg sample	kmol O / m ³ sample
	(m ² /g) / Selectivity (%) ^[b]	mg O / 100 mg sample	mg O / m ² s.a.		kg O / m ³ sample				
1 Ce _{0.91} Mn _{0.09} O ₂	56 / 93	0.07	0.01	4.6	6	0.05	0.3		
2 Ce _{0.90} Bi _{0.10} O ₂	33 / 77	0.46	0.14	32.9	36	0.29	2.2		
3 Ce _{0.90} Cu _{0.10} O ₂	47 / 89	0.12	0.03	7.4	9	0.07	0.6		
4 Ce _{0.90} Fe _{0.10} O ₂	50 / 0	-	-	- ^[d]	-	-	-		
5 Ce _{0.92} Pb _{0.08} O ₂	56 / 92	0.70	0.13	46.1	54	0.44	3.4		
6 Ce _{0.91} Ca _{0.09} O ₂	22 / 0	-	-	-	-	-	-		
7 CeO ₂	38 / 0	-	-	-	-	-	-		
8 CeO ₂ 'C550' ^[e]	84 / 0	-	-	-	-	-	-		
9 Ce _{0.90} Bi _{0.10} O ₂ '400 °C' ^[f]	33 / 98	1.28	0.39	88.9	98	0.80	6.1		
10 Ce _{0.95} Cr _{0.05} O ₂ 'C800' ^[g]	n.d. ^[h] / 91	0.24	n.d.	14.8	18	0.15	1.1		
11 Ce _{0.87} Cr _{0.08} Sn _{0.05} O ₂ /SnO ₂ ^[i]	n.d. / 94	0.52	n.d.	33.1	40	0.32	2.5		
12 Ce _{0.87} Bi _{0.08} Sn _{0.05} O ₂	55 / 84	0.74	0.13	44.6	56	0.46	3.5		
13 (La _{0.7} Sr _{0.3}) _{0.98} MnO ₃	6 / 85	1.12	1.93	71.4	n.d.	0.70	n.d.		
14 La _{0.8} Sr _{0.2} MnO ₃	5 / 92	0.69	1.35	44.1	n.d.	0.43	n.d.		
15 La _{0.9} Sr _{0.1} MnO ₃	3 / 92	0.49	1.58	31.3	n.d.	0.31	n.d.		
16 PbCrO ₄	<1 ^[j] / 100	4.47	-	48.6 ^[k]	282	2.79 ^[l]	17.6		
Ref. CeO ₂ → Ce ₂ O ₃ ^[m]	- / -	4.65	-	-	356	2.91	22.2		

^[a] Conditions: 10 min cycles of 4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 50 mL/min total flow, 550 °C, 250 mg of catalyst (about 0.25 cm³), GHSV 1200 /h. Hydrogen activity is the amount of the hydrogen feed which is combusted during a reduction cycle. ^[b] Selectivity for hydrogen

combustion from a mixture with propene and propane (1:1:4, respectively) at 550 °C, expressed as hydrogen conversion/total conversion. The unselective first data point is not taken into account.^[c] This is the percentage of the hydrogen feed which is combusted by the catalyst during the 10 min reduction cycle.^[d] The unselective catalysts show a net *production* of hydrogen via coking, therefore, their level of hydrogen combustion and selectivity cannot be determined.^[e] This plain ceria sample was calcined at 550 °C instead of 700 °C, resulting in a higher surface area and smaller crystallite size.^[f] This is catalyst **2**, but the catalytic testing was performed at 400 °C instead of 550 °C, which results in a higher selectivity and activity, see Chapter 3.3.^[g] This catalyst was calcined at 800 °C instead of 700 °C, resulting in a larger crystallite size. Traces of Cr₂O₃ were observed by XRD, see Chapter 3.4.^[h] Not determined.^[i] XRD analysis showed that part of the tin is present as a separate SnO₂ phase.^[j] The surface area is too small to be determined.^[k] Note that for this catalyst, ~40 mg instead of 250 mg sample was used. Therefore the percentage hydrogen combusted should not be used to compare the catalysts.^[l] This is the initial activity, after prolonged redox cycling, the activity stabilises at about 25% of this value.^[m] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

II.b Catalyst activity in the mixed dehydrogenation and selective hydrogen combustion process

In the combined dehydrogenation and selective hydrogen combustion process, pure propane is fed over a reactor bed containing a dehydrogenation catalyst and the SOR. Table AII.7 shows how much of the SOR must be added in the reactor to combust 90% of the hydrogen formed in the dehydrogenation reaction, and in case of 10 min reaction cycles (which is similar to the Catofin dehydrogenation process).^[3] A hydrogen conversion of 90% is chosen, since at too low hydrogen levels, hydrocarbon coking will occur. Note that a model study of this process type has been published by De Graaf et al.^[4]

We have used the propane dehydrogenation conditions from data obtained by Grasselli et. al, namely a 0.7 wt % Pt-Sn-ZSM-5 dehydrogenation catalyst, pure propane feed at 2/h WHSV (17 cc propane / g cat /min), and about 25% propane conversion (540 °C).^[5] The selectivity of both catalysts is set to 100%. The activity of the SOR catalyst is based on our measurements in a simulated propane dehydrogenation gas mixture, unless stated otherwise (4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 50 mL/min total flow, 550 °C). Note again that increasing the catalysts surface area can increase the activity, and that the initial activity of the PbCrO₄ catalyst (**16**) is close to the theoretical maximum activity of (doped) ceria.

Table AII.7. The amount of SOR catalyst needed in the combined dehydrogenation and selective hydrogen combustion process.^[a]

Catalyst/ Composition	Weight based		Volume based	
	Amount of SOR needed per kg DH catalyst (kg)	SOR needed (wt %)	Amount of SOR needed per m ³ DH catalyst (m ³)	SOR needed (vol %)
5 Ce _{0.92} Pb _{0.08} O ₂	3.9	80	1.3	56
9 Ce _{0.90} Bi _{0.10} O ₂ ‘400 °C’ ^[b]	2.1	68	0.6	40
15 La _{0.9} Sr _{0.1} MnO ₃	5.5	85	8.7	90
16 PbCrO ₄ ^[c]	0.6	38	0.2	20
Ref. CeO ₂ → Ce ₂ O ₃ ^[d]	0.6	37	0.2	16

^[a] Conditions: 10 min propane dehydrogenation cycles at 540 °C (25% propane conversion), selectivity of both catalyst is 100%, and the SOR combusts 90% of the hydrogen produced. Dehydrogenation catalyst: 0.7 wt % Pt-Sn-ZSM-5, pure propane feed at 2/h WHSV (17 cc propane / g cat /min). The activity of the SOR catalyst is based on our measurements in a simulated propane dehydrogenation gas mixture, unless stated otherwise (4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 50 mL/min total flow, 550 °C). ^[b] This is catalyst **2**, but the catalytic testing was performed at 400 °C instead of 550 °C, see Chapter 3.3. ^[c] These values are based on the initial activity of the catalyst. After prolonged redox cycling, the activity stabilises at about 25% of this value. ^[d] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

Table AII.8 shows the amount of SOR catalyst needed to combust the hydrogen produced by the full dehydrogenation of 1 kg propane. Note that in a real reaction at 550 °C, the propane conversion is about 25%. This means that in this case, one quarter of the amounts of SOR given in Table AII.8 are needed.

Table AII.8. The amount of SOR catalyst needed to combust the hydrogen produced from the dehydrogenation of 1 kg propane.^[a]

Catalyst/ Composition	Weight based (kg)	Volume based (m ³ ·10 ⁻³)
5 Ce _{0.92} Pb _{0.08} O ₂	51.7	6.8
9 Ce _{0.90} Bi _{0.10} O ₂ ‘400 °C’ ^[b]	28.4	3.7
15 La _{0.9} Sr _{0.1} MnO ₃	73.3	46.1
16 PbCrO ₄ ^[c]	8.1	1.3
Ref. CeO ₂ → Ce ₂ O ₃ ^[d]	7.8	1.0

^[a] The activity of the SOR catalyst is based on our measurements in a simulated propane dehydrogenation gas mixture, unless stated otherwise (4:1:1% v/v C₃H₈:C₃H₆:H₂ in Ar at 50 mL/min total flow, 550 °C). ^[b] This is catalyst **2**, but the catalytic testing was performed at 400 °C instead of 550 °C, see Chapter 3.3. ^[c] These values are based on the initial activity of the catalyst. After prolonged redox cycling, the activity stabilises at about 25% of this value. ^[d] Added as reference, this is the maximum of available oxygen from ceria, from the full (surface and bulk) reduction of CeO₂ to Ce₂O₃ (a quarter of the oxygen can be released).

References

- [1] D. Terribile, A. Trovarelli, J. Llorca, C. de Leitenburg and G. Dolcetti, *Catal. Today*, **1998**, 43, 79.
- [2] D. Terribile, A. Trovarelli, J. Llorca, C. de Leitenburg and G. Dolcetti, *J. Catal.*, **1998**, 178, 299.
- [3] T. A. Nijhuis, S. J. Tinnemans, T. Visser and B. M. Weckhuysen, *Chem. Eng. Sci.*, **2004**, 59, 5487.
- [4] E. A. de Graaf, G. Zwanenburg, G. Rothenberg and A. Bliet, *Org. Process. Res. Dev.*, **2005**, 9, 397.
- [5] R. K. Grasselli, D. L. Stern and J. G. Tsikoyiannis, *Appl. Catal. A: Gen.*, **1999**, 189, 9.