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Solid 'oxygen reservoirs' for selective hydrogen oxidation

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Appendix I: Success of doping

The success of doping is determined by XRD and evaluation of the colour of the sample. Doping is considered unsuccessful when a separate dopant-metal or dopant oxide phase is detected by XRD, or when the sample's colour is not homogeneous (spots appear during calcination).

The samples are grouped on the type of dopant, and ordered for increasing dopant concentration (mol%). The type and concentration of the second dopant is added, when applicable. Note that bi-doped samples appear twice in the table, once for each dopant type. Also, doping can be successful for dopant 1, but not for dopant 2 of the same sample. All catalyst were prepared via the standard preparation-method (see below), and calcined at 700 °C, unless stated otherwise.

General procedure for catalyst synthesis. The metal nitrate precursors (or chlorides or ammonium metallates, where nitrates were not available) were weighed into a crucible and placed on a heater. When liquefied, they were mixed with a spatula. If necessary, 2–6 drops of water were added to aid the solution of the precursors. After about 5 minutes, the crucible was placed in a 140 °C vacuum oven. Pressure was reduced to < 10 mbar in about 10 minutes. The latter was performed carefully to prevent vigorous boiling. After 4h, the crucible was placed in a muffle oven and calcined for 5h at 700 °C in static air (ramp rate: 300 °C/h). The resulting solid was pulverized, ground and sieved in fractions of 125–212 µm (selectivity assessment) and < 125 µm (XRD and BET measurements). The final metal concentration was calculated from the amount of precursor weighed in, corrected for the water content as determined on catalysts **G1–01** to **G1–18** by ICP.

Table AI. The success of the synthesis of various doped cerias.

Dopant type	Successful doping		Unsuccessful doping		Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	
Ag			8	Sr, 5	Ag metal
Au			10		Au metal
Al	2				
Al	2	Cu, 2			
Al	2	Cr, 2			
Al	2	Pt, 2			
Al	2	La, 5			
Al	2	Yb, 5			
Al	2	Cu, 5			
Al	2	Bi, 8			
Al	5				
Al	8	Ta, 5			
Al	10				
Bi	2				
Bi	2	Gd, 2			
Bi	2	Mn, 2			
Bi	2	La, 2			
Bi	2.5	Cr, 2.5			
Bi	5	Pt, 5			
Bi	5	Cr, 5			
Bi	5	K, 5			
Bi	5	Cr, 8			
Bi	8				
Bi	8	Cu, 2			
Bi	8	Al, 2			
Bi	8	Sn, 5			
Bi	10				
Ca	2				
Ca	2	Pt, 2			
Ca	2	Sr, 2			
Ca	5	Pb, 5			
Ca	10				
Ca	10	Cu, 5			
Cu	0.1				

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping			Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	Type of extra phase ^[d]	
Cu	1					
Cu	2	Al, 2				
Cu	2	Zr, 2				
Cu	2	K, 2				
Cu	2	Mn, 2				
Cu	2	Ru, 2				
Cu	2	Bi, 8				
Cu	2	W, 8				
Cu	2	Mn, 10				
Cu	3					
Cu	4	Pb, 2.5				
Cu	4	Zr, 4				
Cu	5	Al, 2				
Cu	5	Mn, 2				
Cu	5	Sn, 2				
Cu	5	Gd, 8				
Cu	5	Ca, 10				
Cu	7					
Cu	8					
Cu	8	Mg, 5				
Cu	8	Zr, 8				
Cu	10					
Cu	10	Mn, 2				
Cu			3		CuO	C800
Cu			7		CuO	C800
Cu			8	Mn, 8	Cu-Mn-O	
Cu			8	Sn, 5	CuO	a.m.
Cu			10	Ru, 2	CuO	
Cu			10	Pr, 8	CuO	
Cu			10	Cr, 2	CuO	
Cu			15		CuO	
Cr	2					
Cr	2	Al, 2				
Cr	2	Ta, 5				

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping			Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	Type of extra phase ^[d]	
Cr	2	W, 10				
Cr	2	Cu, 10				
Cr	2	Fe, 10				
Cr	2.5	Bi, 2.5				
Cr	5					a.m., C450
Cr	5					a.m., C550
Cr	5					a.m., C625
Cr	5					a.m., C750
Cr	5					a.m.
Cr	5	Pt, 2				
Cr	5	Zr, 5				
Cr	5	Bi, 5				
Cr	8					
Cr	8					a.m.
Cr	8	Bi, 5				
Cr	8	Sn, 5				a.m.
Cr	8	Fe, 8				
Cr			5			spotted
Cr			5		Cr ₂ O ₃	a.m., C800
Cr			8	Ti, 2	Cr ₂ O ₃	
Cr			8	Ru, 5	Cr ₂ O ₃	
Cr			10		Cr ₂ O ₃	
Fe	2	Zr, 2				
Fe	2	Nd, 8				
Fe	5	Y, 5				
Fe	5	Ru, 5				
Fe	8	Sr, 2				
Fe	8	Mn, 2				
Fe	10					
Fe	10	Cr, 2				
Fe			8	Ti, 2	Fe ₂ O ₃	
Fe			8	Cr, 8	Fe ₂ O ₃	
Gd	2					
Gd	2	Bi, 2				

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping		Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	
Gd	2	Pr, 2			
Gd	2	Mn, 5			
Gd	2	Yb, 5			
Gd	2	Yb, 8			
Gd	5				
Gd	8	Cu, 5			
In			5		In ₂ O ₃
In			10		In ₂ O ₃
K	2				
K	2	Cu, 2			
K	2	Yb, 5			
K	5	Bi, 5			
K	10				
Li			10		Li-oxide
La	2				
La	2	Bi, 2			
La	5	Al, 2			
La	8	Sn, 5			
La	10				
Mg	5	Cu, 8			
Mg	8	Zr, 2			
Mg			10		MgO
Mn	2				
Mn	2	Bi, 2			
Mn	2	Cu, 2			
Mn	2	Cu, 5			
Mn	2	Fe, 8			
Mn	2	Cu, 10			
Mn	5				
Mn	5	Gd, 2			
Mn	5	Sr, 2			
Mn	5	Sr, 5			
Mn			10		Mn ₂ O ₃
Mn			10	Cu, 2	Mn-oxide

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping		Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	
Mn			8	Cu, 8	Cu-Mn-O
Mo			10		Mo-oxide
Ni			10	Sm, 2	Ni-oxide
Nd	2				
Nd	2	Sn, 2			
Nd	8	Fe, 2			
Nd	10				
Pb	2				a.m.
Pb	2.5	Cu, 4			
Pb	8				
Pb	8				a.m.
Pb	8				a.m.
Pb			2		spotted
Pb			2.5	Sr, 4	PbO
Pb			5		PbO
Pb			5	Zr, 2	PbO
Pb			5	Ca, 5	
Pb			5	Sr, 8	PbO
Pb			10		Pb-oxide
Pd	2	Sn, 2			
Pd	5				
Pd	10				
Pr ^[e]	2				
Pr	2	Gd, 2			
Pr	2	W, 2			
Pr	2	Zr, 5			
Pr	8	Cu, 10			
Pt	2				
Pt	2	Al, 2			
Pt	2	Ca, 2			
Pt	2	Mn, 10			
Pt			2	Sn, 2	Pt metal
Pt			2	Cr, 5	Pt metal
Pt			2	W, 8	Pt metal

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping			Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	Type of extra phase ^[d]	
Pt			5	Bi, 5	Pt metal	
Ru	2					
Ru	2	Cu, 2				
Ru	2	Cu, 10				
Ru	5					
Ru	5	Cr, 8				
Ru	5	Sm, 5				
Ru			5	Fe, 5	RuO ₂	
Ru			8		RuO ₂	
Sm	2	Ni, 10				
Sm	5	Ru, 5				
Sn	2					
Sn	2	Nd, 2				
Sn	2	W, 2				
Sn	2	Pd, 2				
Sn	2	Pt, 2				
Sn	5	Bi, 8				
Sn	5	La, 8				
Sn	8					a.m.
Sn			2	Cu, 5	SnO ₂	
Sn			5	Cr, 8	SnO ₂	a.m.
Sn			5	Cu, 8	SnO ₂	a.m.
Sn			10		Sn oxide	
Sr	2					
Sr	2	Mn, 5				
Sr	2	Ca, 2				
Sr	4	Pb, 2.5				
Sr	5					
Sr	5	Mn, 5				
Sr	5	Y, 5				
Sr	5	Ag, 8				
Sr	8	Pb, 5				
Sr			2	Zr, 5	Sr(CeO ₃)	
Sr			10		Ce-Sr-O	

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping		Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	
Ta			2		Ta ₂ O ₅
Ta			5	Ti, 5	Ta ₂ O ₅
Ta			5	Cr, 2	Ta ₂ O ₅
Ta			5	Ti, 8	Ta ₂ O ₅
Ti	2				
Ti	2	Fe, 8			
Ti	2	Cr, 8			
Ti	5	Ta, 5			
Ti	8				
Ti	8	Ta, 5			
V			8	Mo, 8	V-oxide
W	2				
W	2	Sn, 2			
W	2	Pr, 2			
W	10	Cr, 2			
W			2		W-oxide
W			8	Cu, 2	W-oxide
W			8	Pt, 2	W-oxide
W			10		W-oxide
Y	2				
Y	5				
Y	5	Fe, 5			
Y	5	Sr, 5			
Yb	2				
Yb	5	K, 2			
Yb	5	Al, 2			
Yb	5	Gd, 2			
Yb	8	Gd, 2			
Yb	10				
Zr	2				
Zr	2	Fe, 2			
Zr	2	Cu, 2			
Zr	2	Pb, 5			
Zr	2	Fe, 8			

Table AI, continued.

Dopant type	Successful doping		Unsuccessful doping		Comments [a,b,c]
	Conc. (mol%)	Second dopant, conc. (mol%)	Conc. (mol%)	Second dopant, conc. (mol%)	
Zr	2	Mg, 8			
Zr	4	Cu, 4			
Zr	5	Pr, 2			
Zr	5	Sr, 2			
Zr	5	Cr, 5			
Zr	8				
Zr	8	Cu, 8			
Zr	10				

^[a] a.m. : the sample is made with the adjusted preparation method described in chapter 2.3. The difference with the standard preparation method is that the dopant precursors are placed in a crucible without adding the cerium nitrate, and dissolved in as little water as possible. Then, the cerium nitrate is added and mixed with the dissolved dopant precursor(s) into a slurry. This is heated on a heating plate until the cerium nitrate melts, and then placed in a vacuum oven. In the standard preparation method, the dopant precursors and the cerium nitrate are both placed in a crucible, mixed, and heated on a heating plate. If one of the precursors does not melt or dissolve, a few drops of water are added, and the mixture is placed in a vacuum oven. ^[b] C[value] means that the sample is not calcined at 700 °C but at the value given. ^[c] 'Spotted' means that no XRD was performed since the colour of the sample was not homogeneous after calcination, indicating an extra phase has formed. ^[d] Determined by XRD. If the precise phase cannot be detected, the extra phase is labelled 'dopant-oxide'. ^[e] The XRD peaks of ceria and Pr-oxide are similar, so it is hard to determine if a separate dopant phase has formed.