

Figure SI1. Simplified block diagram of the test rig



Figure SI2. Overview image of the EDX line scan



Figure SI3. CO conversion graphs, dry fuel gas (FG1) & moist fuel gas (FG2) with Monolith #2 (CuO/CeO<sub>2</sub>), all  $\lambda$  = 2.5, varying GHSV.



Figure SI4. CO conversion graphs, comparing single coated monolith #1 and double coated monolith #2 (CuO/CeO<sub>2</sub>), all  $\lambda$  = 2.5, varying GHSV.

## Table SL1. Monoliths overview

		preparation/ coating method				monolith				Feed [mol.%]														
composition	Washcoat carrier		layer [μm]	pore size [nm]	coating quantity [mg/cm³]	support	l [mm]	D [mm]	V [cm <sup>3</sup> ]	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CO	N <sub>2</sub>	O <sub>2</sub>	GHSV [h <sup>-1</sup> ]	λ	T [°C]	X(CO) [%]	S(CO) [%]	X(O <sub>2</sub> ) [%]	Y(CO) [%]	remark	ref.
5 wt.% Pt, 0.5 wt.% Fe	Al <sub>2</sub> O <sub>3</sub>	dip-coating	15 - 20	-	Al <sub>2</sub> O <sub>3</sub> : 98 Pt: 4.9 Fe: 0.49	honeycomb ceramic 400 cpsi	50,8	25,4	25.7	42.0	9.0	12.0	1	35 - 35.75	0.25 - 1.0	10000	2.0	100 at inlet	47	40	100	18,8		[1]
unknown, propietary Engelhard Selectra-PROX I	-	-	-	-	-	honeycomb cordierite, 600 cpsi	127	76,2	579	38.4	19.9	16.8	0.2	24.7		18000	1.35			69	100			[2]
0.5 wt.% Pt	Al <sub>2</sub> O <sub>3</sub>	-	-	-	-	cordierite 600 cpsi	-	-	-	30.0	17.0	15.0	0.003 - 1.0	balance	0.003 - 1.0	-	-	-	-	-	-	-		[3]
0.5 wt.% Pt																10000 30000		170 180	99 95	50 61	100 100	50 58		
0.5 wt.% Pd	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	impregnation	-	-	-	honeycomb cordierite	-	-	-	40.0	-	20.0	0.8	38.4	0,8	30000	2.0	240-280	25	12	100	3		[4]
0.5 wt.% Rh						400 CpSi										30000		120-150	68	35	100	24		
0.5 wt.% Ru																30000		130	52	27	100	14		
0.1 wt.% Pt	12 % γ-Al <sub>2</sub> O <sub>3</sub>	dip-coating slurry-sol-slurry	-	-	-	honeycomb metallic Fe-20Cr-5Al 400 cpsi	-	-	-	39.6	19.8	16.5	1.0	22.1	1.0	10000	2.0	198-206	96	47,5	-	46	i	[5]
4 wt.% Pt, 0.5 wt.% Fe, Mordenite	-	dip-coating	14		100	honeycomb cordierite, 400 cpsi	15	12	1.70	63.0	20.0	15.0	1.0	-	1.0	9500	2.0	100-150	99,95	50	100	50,0		[6]
15 mol.% Cu, 85 mol.% Ce			-	-	-													165-185	100	70	100	70,0	)	
15 mol.% Cu, 8.5 mol.% Nd,			-	-	-	honeycomb metallic	45	-	0			10.0	0.5	24 5	o -		2.0	165-205				70,0	1	()
76.5 mol.% Ce 15 mol % Cu_ 8 5 mol % 7r	Al <sub>2</sub> O <sub>3</sub>	dip-coating				Fe-20Cr-5Al 400 cpsi	15	/	0.577	50.0	7.5	10.0	0.5	31.5	0.5		2.0		100	70		,		[/]
76.5 mol.% Ce			-	-	-													165-205	100	75		75 <i>,</i> 0		
		dip-coating			100	honeycomb												130	99.9	-	-	0.0	after 200 h	
4 wt.% Pt, 0.5 wt.% Fe, Mordenite	-	alumina-sol	-	-		cordierite, 400 cpsi	15	12	1.70	73.0	0 20.0	5.0	1.0	-	1.0	9500	2.0	100				H <sub>2</sub> O-tr	H <sub>2</sub> O-tolerance	[8]
		dip-coating silica-sol			100	honeycomb cordierite, 400 cpsi												100	99.8	-	-	0.0	0.0 durability test	
2 wt.% Pt, Z-PM zeolith		impregnation.				honevcomb		-										100-150	65	>50	-	-	coating quantity	
2 wt.% Pt,SiO <sub>2</sub>	-	dip-coating	50 - 75	-	50	cordierite, 225 cpsi	-		-	97.5	-	-	1.0	-	1.5	225000	3.0	250	82	52	-	-	approximated	[9]
1 wt.% Pt	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	imprognation	-	3.8	-	macro-porous				50.0			1.0	) 48.0	1.0	20000	2.0	225-250	99.6	42	100	41.8		[40]
1 wt.% Pt, 2 wt.% K	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Impregnation	-	3.0	-	Al <sub>2</sub> O <sub>3</sub>	-	-	-	50.0	-	-	1.0			20000	2.0	200-250	>99	42	100	41.6	molar ratio K/Pt = 10	[10]
1 wt.% Pt, 1.5 wt.% Ni	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	impregnation	-	-	-	macro-porous Al <sub>2</sub> O <sub>3</sub>	-	-	-	50.0	12.5	15.0	1.0	20.5	1.0	16000	2.0	140-180	>99	51	-	51		[11]
CuO-CeO <sub>2</sub> (6.8 wt.% Cu)			9	4.5	-	honeycomb												135-158	100	-	-	-	Cu/Ce-ratio=0.13	
CuO-CeO₂ (8.6 wt.% Cu)	-	impregnation	12	44	-	cordierite, 400 cpsi	21	9	1.34	42.0	15.0	15.0	0.7	He 26.6	0.7	9000	2.U 128-14	128-144	100	-	-	-	Cu/Ce-ratio=0.17	[12]
M1 Co-ZrO <sub>2</sub> (15.9 wt.% Co)			-	-	41													250-260	70	-	-	-	slurry ZrO <sub>2</sub> , 10wt.%/HA	2
M2 Co-ZrO <sub>2</sub> (12.1 wt.% Co)			-	-	35													-	-	-	-	-	slurry ZrO <sub>2</sub> , 10wt.%/H <sub>2</sub> C	)
M3 Co-ZrO <sub>2</sub> (11.1 wt.% Co)			-	-	40													250-260	85	-	-	-	slurry ZrO <sub>2</sub> , 20wt.%/HA	2
M3* Co-ZrO <sub>2</sub> (21.5 wt.% Co)			-	-	38													240	90	-	-	-	slurry ZrO <sub>2</sub> , 20wt.%/HA	2
	ZrO <sub>2</sub>	impregnation	_	_		honeycomb	20	10x10	2.00	40.0	-	-	1.0	He 58.0	1.0	-	2.0			_	_	_	slurry NYACOL(ZrO <sub>2</sub> ),	[13]
M4 Co-ZrO <sub>2</sub> (10.6 wt.% Co)					76													220-250	>90				stability test 100h	
M5 Co-ZrO <sub>2</sub> (10.6 wt.% Co)			-	-	55													240-260	85	-	-	-	20wt.%/NYACOL(ZrO <sub>2</sub> )	
			-	-																-	-	-	slurry NYACOL(Al <sub>2</sub> O <sub>3</sub> )-	
$\frac{1}{10000000000000000000000000000000000$			-		66													-	-				2rU2 20 WT.%/HAC	
$C1 C0 - CeO_2 (11.2 \text{ wt.% C0})$	CeOa	impregnation	-	-	23	honeycomb	20	10v10	2 00	<u>40 0</u>	_	_	10	He 58 0	1 0	_	20	200-210	98	-	-	-		[1/1]
$C_2 = C_0 - C_0 C_2 (10.1 \text{ W} 1.\% \text{ C} 0)$		mpregnation	-	-	55	cordierite, 400 cpsi	20	10/10	2.00	-10.0			1.0	110 50.0	1.0		2.0	200-210	95	-	-	-	coating quantity	[14]
0.02 wt % Pt 4.5 wt % CuO	CeOa	SERD	-		23		_			<u>/</u> 10	-	_	0 5	58 በ	0.5		2.0	200-210	20				calculated	[15]
5.52 WL./0 L L, T.J WL./0 CUU		5110	-							-1.U			0.0	0.00	0.5		2.0	120	~90					[-]

						monolith				Feed [mol.%]														
composition	Washcoat carrier	preparation/ coating method	layer [µm]	pore size [nm]	coating quantity [mg/cm³]	support	l [mm]	D [mm]	V [cm³]	H <sub>2</sub>	CO <sub>2</sub>	H₂O	CO	N <sub>2</sub>	O <sub>2</sub>	GHSV [h <sup>-1</sup> ]	λ	т [°С]	X(CO) [%]	S(CO) [%]	X(O₂) [%]	Y(CO) [%]	remark	ref.
0.01 wt.% Pt, 2.0 wt.% CuO	CeO <sub>2</sub>	SFRD				α-Al <sub>2</sub> O <sub>3</sub> -												140-150	>90	-	-	-	SFRD supercritical	
0.03 wt.% Pt, 5.8 wt.% CuO	CeO <sub>2</sub>	SFRD				foam, 20 ppi												90-150	<60	-	-	-	fluid reactive deposition	
1.0 wt.% Au, 1.25 wt.% MgO	$AI_2O_3$	homogenous deposition- precipitation (urea)	-	-	-	honeycomb cordierite	20	11	1.90	61.7	-	-	1.0	He 36.3	1.0	-	3.2	90	60	-	-	-	·	[16]
Pt-promoted CuFe-catalyst*	Al <sub>2</sub> O <sub>3</sub>	impregnation	-	-	-	honeycomb cordierite, 400 cpsi	76.2	19.1	21.7	45.7	17.5	25.0	0.222	11.4	0.222	24000	2.0	70-150	>96	>50	-	>48	propietary	[17]
CuO <sub>x</sub> -CeO <sub>2</sub> (14 mol.% Cu, 86 mol.% Ce)	enamel	coprecipitation	-	8	10	a enameled 3 steel monolith	30	17	6.81	50.0	-	-	1.0	48.0	1.0	7000	2.0	170-200	>99	-	-	-		[18]
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO)	-	wet impregnation, dip-coating	12-15	-	23	0 honeycomb cordierite, 900 cpsi	12	16	2.41	50.0	- 15	- 10	0.5	48.6 23.6	0.9	-	3.6	90-120 145	>95 >90	30-60 <30	-	30-60 <30		[19]
2 wt.% Au/TiO <sub>2</sub>		incipient wetness impregnation			23.	0 anodized Al- monolith	15	14	2.31			con	nposition not	given		1040	3.0	80-110	50	<20	-	<10		[20]
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO), S1-M		wet impregnation, dip-coating	15			honeycomb cordierite, 400 cpsi	12	16	2.41	50.0	-	-	0.5	23.6	0.9		3.6	140-200	>99	28-62	-	28-80		
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO), S2-M		wet impregnation, dip-coating	15			honeycomb cordierite, 400 cpsi	12	16	2.41	50.0	-	-	0.5	23.6	0.9		3.6	160-180	>99	33-48	-	28-80		
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO), S3-M		wet impregnation, dip-coating	15			honeycomb cordierite, 400 cpsi	12	16	2.41	50.0	-	-	0.5	23.6	0.9		3.6	140-200	>99	28-78	-	28-80		[21]
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO), S5-M		wet impregnation, dip-coating	15			honeycomb cordierite, 400 cpsi	12	16	2.41	50.0	-	-	0.5	23.6	0.9		3.6	130-200	>99	28-87	-	28-80		
CuO <sub>x</sub> -CeO <sub>2</sub> (4.2 wt.% CuO), S6-M		wet impregnation, dip-coating	15			honeycomb cordierite, 400 cpsi	12	16	2.41	50.0	-	-	0.5	23.6	0.9		3.6	200	98	31	-	28-80		
CuO (4.8 wt.% Cu)	CeO <sub>2</sub>	wet impregnation, dip-coating			28.	9 3d-printed resin	10	15	1.77	30.0	-	-	2.0	He 66.0	2.0	2000	2.0	135	95	90	-	86	10 h experiment	[22]
CuO-CeO <sub>2</sub> /celite (CuO 4.6 wt.%, CeO <sub>2</sub> 18.7 wt.%, Cu/Ce=0.55)		co-impregnation, dip-coating	20-30		4	6												150-185	>98					
CuO-CeO <sub>2</sub> /aerosil (CuO 4.9 wt.%, CeO <sub>2</sub> 18.9 wt.%, Cu/Ce=0.55)		co-impregnation, dip-coating	20-30		4	7 honeycomb 7 cordierite, 400 cpsi	10	10x10	1.0									185	91					[23]
CuO-CeO <sub>2</sub> /SBA-15 (CuO 4.9 wt.%, CeO <sub>2</sub> 19.1 wt.%, Cu/Ce=0.55)		co-impregnation, dip-coating	20-30		4	8												185	85					

## References Supplementary Table1 Monoliths overview

G.W. Roberts, P. Chin, X. Sun, J.J. Spivey, Preferential oxidation of carbon monoxide with Pt/Fe monolithic catalysts: Interactions between external transport and the reverse water-gas-shift reaction, Appl. Catal., B, 46 (2003) 601-611. <u>http://dx.doi.org/10.1016/j.apcatb.2003.07.002</u>.
 R.K. Ahluwalia, Q. Zhang, D.J. Chmielewski, K.C. Lauzze, M.A. Inbody, Performance of CO preferential oxidation reactor with noble-metal catalyst coated on ceramic monolith for on-board fuel processing applications, Catal. Today, 99 (2005) 271-283.

http://dx.doi.org/10.1016/j.cattod.2004.10.015.

[3] E.J. Bissett, S.H. Oh, R.M. Sinkevitch, Pt surface kinetics for a PrOx reactor for fuel cell feedstream processing, Chem. Eng. Sci., 60 (2005) 4709-4721. <u>http://dx.doi.org/10.1016/j.ces.2005.02.069</u>.

[4] S. Zhou, Z. Yuan, S. Wang, Selective CO oxidation with real methanol reformate over monolithic Pt group catalysts: PEMFC applications, Int. J. Hydrog. Energy, 31 (2006) 924-933.

http://dx.doi.org/10.1016/j.ijhydene.2005.07.014.

[5] J. Zhang, J. Jia, C. Zhang, S. Wang, Preparation of Pt/Al<sub>2</sub>O<sub>3</sub> Metallic Honeycomb Catalyst and Its Catalytic Properties for CO Preferential Oxidation, Chin. J. Catal., 29 (2008) 421-425. https://www.cjcatal.com/EN/Y2008/V29/I5/421.

[6] N. Maeda, T. Matsushima, H. Uchida, H. Yamashita, M. Watanabe, Performance of Pt-Fe/mordenite monolithic catalysts for preferential oxidation of carbon monoxide in a reformate gas for PEFCs, Appl. Catal., A, 341 (2008) 93-97. <u>http://dx.doi.org/10.1016/j.apcata.2008.02.022</u>.

[7] S.H. Zeng, Y. Liu, Nd- or Zr-modified CuO-CeO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> /FeCrAl monolithic catalysts for preferential oxidation of carbon monoxide in hydrogen-rich gases, Appl. Surf. Sci., 254 (2008) 4879-4885. http://dx.doi.org/10.1016/j.apsusc.2008.01.168.

[8] N. Maeda, T. Matsushima, M. Kotobuki, T. Miyao, H. Uchida, H. Yamashita, M. Watanabe, H<sub>2</sub>Otolerant monolithic catalysts for preferential oxidation of carbon monoxide in the presence of hydrogen, Appl. Catal., A, 370 (2009) 50-53. <u>http://dx.doi.org/10.1016/j.apcata.2009.09.010</u>.

[9] G. Neri, G. Rizzo, F. Corigliano, I. Arrigo, M. Caprì, L. De Luca, V. Modafferi, A. Donato, A novel Pt/zeolite-based honeycomb catalyst for selective CO oxidation in a H<sub>2</sub>-rich mixture, Catal. Today, 147 (2009) S210-S214. http://dx.doi.org/10.1016/j.cattod.2009.07.049.

[10] Y. Zhang, C.Y. Zhao, H. Liang, Y. Liu, Macroporous monolithic Pt/γ-Al<sub>2</sub>O<sub>3</sub> and K-Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts used for preferential oxidation of CO, Catal. Lett., 127 (2009) 339-347. http://dx.doi.org/10.1007/s10562-008-9686-z.

[11] S. Lu, Y. Liu, Y. Wang, Meso-macro-porous monolithic Pt-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts used for miniaturizing preferential carbon monoxide oxidation reactor, Chem. Commun., 46 (2010) 634-636. http://dx.doi.org/10.1039/b912769k.

[12] J.L. Ayastuy, N.K. Gamboa, M.P. González-Marcos, M.A. Gutiérrez-Ortiz, CuO/CeO<sub>2</sub> washcoated ceramic monoliths for CO-PROX reaction, Chem. Eng. J., 171 (2011) 224-231. <u>http://dx.doi.org/10.1016/j.cej.2011.03.006</u>.

[13] L.E. Gómez, I.S. Tiscornia, A.V. Boix, E.E. Miró, Co/ZrO<sub>2</sub> catalysts coated on cordierite monoliths for CO preferential oxidation, Appl. Catal., A, 401 (2011) 124-133. http://dx.doi.org/10.1016/j.apcata.2011.05.007.

[14] L.E. Gómez, I.S. Tiscornia, A.V. Boix, E.E. Miró, CO preferential oxidation on cordierite monoliths coated with Co/CeO<sub>2</sub> catalysts, Int. J. Hydrog. Energy, 37 (2012) 14812-14819. http://dx.doi.org/10.1016/j.ijhydene.2012.01.159.

[15] S. Lang, M. Türk, B. Kraushaar-Czarnetzki, Novel PtCuO/CeO<sub>2</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sponge catalysts for the preferential oxidation of CO (PROX) prepared by means of supercritical fluid reactive deposition (SFRD), J. Catal., 286 (2012) 78-87. <u>http://dx.doi.org/10.1016/j.jcat.2011.10.017</u>.

[16] S. Özdemir, Z.I. Önsan, R. Yildirim, Selective CO oxidation over monolithic Au-MgO/Al<sub>2</sub>O<sub>3</sub> catalysts, J. Chem. Technol. Biotechnol., 87 (2012) 58-64. <u>http://dx.doi.org/10.1002/jctb.2682</u>.
[17] Q. Zhang, L. Shore, R.J. Farrauto, Selective CO oxidation over a commercial PROX monolith catalyst for hydrogen fuel cell applications, Int. J. Hydrog. Energy, 37 (2012) 10874-10880. http://dx.doi.org/10.1016/j.ijhydene.2012.04.032.

[18] M.I. Domínguez, A. Pérez, M.A. Centeno, J.A. Odriozola, Metallic structured catalysts: Influence of the substrate on the catalytic activity, Appl. Catal., A, 478 (2014) 45-57. http://dx.doi.org/10.1016/j.apcata.2014.03.028. [19] P.S. Barbato, A. Di Benedetto, G. Landi, L. Lisi, CuO/CeO<sub>2</sub> based monoliths for CO preferential oxidation in H<sub>2</sub>-rich streams, Chem. Eng. J., 279 (2015) 983-993. https://dx.doi.org/10.1016/j.cej.2015.05.079.

[20] E. Adrover, D. Boldrini, N.J. Divins, A. Casanovas, G. Tonetto, E. López, J. Llorca, Study of Cu-Zn and Au/TiO<sub>2</sub> catalysts on anodized aluminum monoliths for hydrogen generation and purification, Int. J. Chem. Reactor Eng., 14 (2016) 831-842. <u>http://dx.doi.org/10.1515/ijcre-2015-0119</u>.

[21] G. Landi, Barbato, Paola Sabrina, A. Di Benedetto, L. Lisi, Optimization of the preparation method of CuO/CeO<sub>2</sub> structured catalytic monolith for CO preferential oxidation in H<sub>2</sub>-rich streams, Appl. Catal., B, 181 (2016) 727-737. <u>https://dx.doi.org/10.1016/j.apcatb.2015.08.040</u>.

[22] C.Y. Chaparro-Garnica, A. Davó-Quiñonero, E. Bailón-García, D. Lozano-Castelló, A. Bueno-López, Design of Monolithic Supports by 3D Printing for Its Application in the Preferential Oxidation of CO (CO-PrOx), ACS Applied Materials & Interfaces, 11 (2019) 36763-36773.

http://dx.doi.org/10.1021/acsami.9b12731.

[23] I.S. Tiscornia, A.M. Lacoste, L.E. Gómez, A.V. Boix,  $CuO-CeO_2/SiO_2$  coating on ceramic monolith: Effect of the nature of the catalyst support on CO preferential oxidation in a H<sub>2</sub>-rich stream, Int. J. Hydrog. Energy, 45 (2020) 6636-6650. <u>http://dx.doi.org/10.1016/j.ijhydene.2019.12.126</u>.