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Supplementary Information

Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes

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Table S1 Compilation of literature reports on photocatalytic CO_2 reduction. Numbers marked are discussed in more detail.

year	Catalysts	loading	primary products	product yield: methane	product yield: methanol	quantum yield	reactor/sample cell	reactants	T / K.	light source	light intensity	reference
1978*	p type-GaP(WE); n type-TiO_2(CE)		HCHO, HCOOH, CH_3OH	-	1.88(μmol/h)			CO_2 in $Li_2CO_{3(aq)}$	298	Hg lamp	210mW/cm^2	Halmann et al.[128]
1979*	SiC		HCHO, CH_3OH	-	76.4(μmol/g-cat/h)	0.45% (CH_3OH)	glass cell,	CO_2 in H_2O	-	500W Xe/Hg lamp		Inoue et al.[129]
	TiO_2			-	4.86	0.019	quartz window					
	GaP			-	15.7	-						
	CdS			-	16.7	-						
	WO_3				0	-						
1987	Ru/TiO_2	3.8wt%	CH_4	1.7(μmol/g-cat/h)	-		pyrex cell	CO_2, H_2O (1:12)	298	solar simulator	80mW/cm^2	Thampi et al.[130]
				51.78	-				319			
				105	-				363			
				2.7	-				298	150W Xe lamp+ filter		
	Ru/TiO_2 - no illumination	3.8		1.7	-				319	(λ<435nm)		
1992*	TiO_2(anatase, Furuuchi) + Cu(Wako)	0.5g TiO_2 + 0.3g Cu	CO, HCHO, HCOOH, CH_3OH	-	0.56(μmol/g-cat/h)		cylindrical pyrex cell	CO_2 in H_2O	313	500W Xe lamp		Hirano et al.[131]
				0.05(μmol/g-cat/h)	1.32			CO_2 in $KHCO_{3(aq)}$				
1993*	Degussa P25 TiO_2	-	CH_4, C_2H_6, CH_3OH, HCOOH, CH_3COOH	0.93(μmol/g-cat/h)	Trace		quartz cell	CO_2 in H_2O	278	500W Hg lamp		Ishitani et al.[132]
	Pd-TiO_2	2wt%		32.93	Trace					(λ>310nm)		
	Rh-TiO_2	2		13.33	Trace							
	Pt-TiO_2	2		6.67	Trace							
	Au-TiO_2	2		4.4	Trace							
	Cu-TiO_2	2		2.53	Trace							
	Ru-TiO_2	2		0.8	Trace							
1995	TiO_2(100) (rutile single crystal on wafer)	-	CH_4, CH_3OH	3.5(μmol/g-cat/h)	2.4(μmol/g-cat/h)		quartz cell	CO_2, H_2O (1:3)	275	75W Hg lamp		Anpo et al.[133]
	TiO_2(110)	-		0	0.8					(λ>280nm)		
	TiO_2 anchored on porous Vycor glass	-		0.02	-			CO_2, H_2O (1:5)				
1995	Ti-ZSM-5(ion exchange)	10wt%	CO, CH_4, CH_3OH	0.03(μmol/g-cat)	-			H_2O/CO_2=5 (at most)	323	75W Hg lamp		Yamashita et al.[134]
	Ti-ZSM-5(anchored)	10		0.01	-					(λ>280nm)		
	Ti-Y(ion exchange)	10		0.2	0.13(μmol/g-cat)							
	Ti-PVG(anchored)	10		0.17	0.03							
1995	Degussa P25 TiO_2	-	H_2, CO, CH_4	2(μmol/g-cat/h)	-		quartz cell	CO_2, H_2O	343	1000W Hg lamp		Saladin et al.[135]
										(λ<700nm)		
1997	TiO_2(anatase, 500m^2/g)	-	H_2, CH_4, C_nH_m	3.75(μmol/g-cat/h)	-		miniaturized photoreactor	CO_2, H_2O	373	200W Hg/Xe lamp		Saladin et al.[136]
	Degussa P25 TiO_2	-		4.74	-				298	(λ<900nm)		
		-		5.68	-				373			
		-		6.42	-				473			
1998*	Degussa P25 TiO_2	-	CH_4, HCOOH	0.43			stainless steel vessel	CO_2 in iso-propyl alcohol		4200W Xe lamp	62mW/cm^2	Kaneco et al.[137]

				product yield								
year	catalysts	loading	primary products	methane	methanol	quantum yield	reactor/sample cell	reactants	temp.	light source	light intensity	reference
1998	Pt-Ti/MCM-48	80 (Si/Ti)	CH_4, CH_3OH	12.3(μmol/g-TiO_2/h)	0.2(μmol/g-TiO_2/h)		quartz cell	CO_2, H_2O (1:5)	328K	Hg lamp (λ>280nm)		Yamashita
	Ti-MCM-48	80 (Si/Ti)		7.6	3							et al.[138]
	Ti-MCM-41	100 (Si/Ti)		3.6	1.36							
	TS-1	85 (Si/Ti)		2.7	0.6							
	Pt-ion-ex-TiOY	1wt%Pt; 1.1wt%Ti		12.4	1.12							
	ion-ex-TiOY	1.1wt%Ti		7.2	4.8							
	imp-TiO_2/Y(SiO_2/Al_2O_3=5.5)	1wt%Ti		5	0.34							
	imp-TiO_2/Y(SiO_2/Al_2O_3=5.5)	10wt%Ti		1.2	-							
	TiO_2(JRC-TIO-4)(92%anatase,8%rutile)	-		0.34	-							
1999*	TiO_2/Pd/SiO_2	10wt%TiO_2	CH_4, HCHO, HCOOH,	0.8(μmol/h)	2.5(μmol/h)		batch type reactor	CO_2 in $KHCO_{3(aq)}$		250mW Hg lamp		Subrahmanyam
	Li-TiO_2/Al2O_3		CH_3OH, C_2H_5OH	2.5	0.8							et al.[139]
2001	TiO_2/FSM-16(physical mix)	1wt%Ti	CH_4, CH_3OH	127(μmol/g-cat/h)	5.4(μmol/g-cat/h)		quartz cell	CO_2, H_2O (1:5)	323K	100W Hg lamp		Ikeue et al.[140]
	imp-Ti/FSM-16	1		207	10.8					(λ>250nm)		
	anc-Ti/FSM-16(anchoring with TPOT)	1		270	35							
	Ti-FSM-16(direct synthesis)	1		259	40.5							
2001	Ti-Beta(F)	2wt%Ti	CH_4, CH_3OH	0.7(μmol/g-Ti/h)	0.47(μmol/g-Ti/h)		quartz cell	CO_2, H_2O (1:5)	323K	75W Hg lamp		Ikeue et al.[141]
	Ti-Beta(OH)	2	CH_4, CH_3OH	5.76	1.35					(λ>250nm)		
	TS-1	-	CH_4, CH_3OH	1.29	0.41							
	Degussa P25 TiO_2	-	CH_4	0.35	-							
2002*	Degussa P25 TiO_2	-	CH3OH	-	6.37(μmol/g-cat/h)	3.41% (CH_3OH)	inner-irradiated cell	CO_2 in $NaOH_{(aq)}$	323K	8W Hg lamp	0.138mW/cm^2	Tseng et al.[142]
	TiO_2	-		-	0.78	0.42				(λ=254nm)		
	Cu/P25 TiO_2	2wt%		-	10	5.35						
	Cu/TiO_2	2		-	19.75	10.02						
2002	Ti-containing nanoporous silica films (Ti-PS)						quartz cell	CO_2, H_2O (1:5)	323K	100W Hg lamp	0.265mW/cm^2	Ikeue et al.[143]
	Ti-PS film(c,50)	50 (Si/Ti)	CH_4, CH_3OH	1.2(μmol/g-Ti/h)	1.7(μmol/g-Ti/h)	0.07%				(λ>250nm)		
	Ti-PS film(h,25)	25		4.2	0.2	0.17						
	Ti-PS film(h,50)	50		7.1	1.8	0.28						
	Ti-PS powder(h,50)	50		3.6	0.85							
	Ti-MCM-41 powder	100		3	1.3							
2003	Fe-Cu-K/DAY and Pt/$K_2Ti_6O_{10}$ (1:1)		H_2, HCHO, HCOOH,	0.013(μmol/g-cat/h)	-		optical quartz tube cell	CO_2, H_2O	298K	300W Xe arc lamp	-	Guan et al.[144]
			CH_4, CH_3OH, C_2H_5OH	0.05	-				298	150W Hg lamp	-	
				0.047	4.83(μmol/g-cat/h)				590	concentrated sunlight	62mW/cm^2	
				0.043	2.3				562	concentrated sunlight	72mW/cm^2	
				0.037	Trace				534		101mW/cm^2	
2004*	TiO_2(anatase, Aldrich)		CH_4	0.88(μmol/g-TiO_2/h)	-		Rayonet photoreactor	CO_2 in H_2O	298K	350nm light source		Dey et al.[145]
				0.84	-			CO_2 in 0.05M 2-propanol				
				2.16	-			CO_2 in 0.5M 2-propanol				
2004*	Cu/TiO_2($CuCl_2$-0hr)	2wt%Cu	CH_3OH	-	23.33(μmol/g-cat/h)		cylindrical quartz reactor	CO_2 in $NaOH_{(aq)}$		UVC (λ=254nm)		Tseng et al.[146]
	Cu/TiO_2($CuCl_2$-0hr)	2		-	6.67							
	Cu/TiO_2($CuCl_2$-8hr)	2		-	0.33					UVA (λ=365nm)		

year	catalysts	loading	primary products	product yield: methane	product yield: methanol	quantum yield	reactor/sample cell	reactants	temp.	light source	light intensity	reference
2004*	Cu/TiO_2	2wt%	CH_3OH		16.7(μmol/g-cat/h)		cylindrical quartz reactor	CO_2 in $NaOH_{(aq)}$	323K	8W Hg lamp		Tseng et al.[147]
	Ag/TiO_2	2			14.3					(λ=254nm)		
2004*	TiO_2/Nafion film	10wt%TiO_2/g-Nafion	HCOOH, CH_3OH,	-	56(μmol/g-TiO_2/h)		flow system,	liquid CO_2	-	990W Xe arc lamp		Pathak et al.[124]
	Degussa P25 TiO_2	-	CH_3COOH	-	1.8		quartz window					
2004*	P-25(1gTiO2/L sol.)		CH_4, CH_3OH	-	93.75(μmol/g-cat/h)		inner-irradiated cell	$NaHCO_{3(aq)}$		15W UV lamp (365nm)	1.3mW/cm^2	Ku et al.[148]
2005	Ti-MCM-41	100 (Si/Ti)	CH_4, CH_3OH	2.99(μmol/g-Ti/h)	1.33(μmol/g-Ti/h)		quartz cell	CO_2, H_2O (1:5)	323K	100W Hg lamp		Hwang et al.[149]
	Ti-MCM-48	80		7.57(μmol/g-Ti/h)	3.06(μmol/g-Ti/h)					(λ>250nm)		
	Ti-SBA-15	270		106(μmol/g-Ti/h)	27.7(μmol/g-Ti/h)							
	TS-1	85		2.6(μmol/g-TiO_2/h)	0.6(μmol/g-TiO_2/h)							
	Degussa P25 TiO_2	-		0.33(μmol/g-Ti/h)	0.005(μmol/g-Ti/h)							
2005	Cu/TiO_2	0.52wt%Cu	CH_3OH		0.18(μmol/g-cat./h)		optical fiber photoreactor	CO_2, H_2O (50:1)	348K	Hg lamp (λ=365nm)	13500mW/cm^2	Wu et al.[126]
		1.2			0.42							
		2.06			0.35							
2006*	Ru/TiO_2	0.5wt%Ru	CH_4, CH_3OH	205.4(μmol/g-Ti)	13.8(μmol/g-Ti)		inner-irradiated cell	CO_2 in H_2O		1000W Hg lamp		Sasirekha et al.[150]
	TiO_2/SiO_2	10wt%Ti		267.7	80.7					(λ=365nm)		
	Ru-TiO_2/SiO_2	0.5wt%Ru; 10wt%Ti		223.8	43.8							
	TiO_2(99%, Lancaster)	-		184.6	11.9							
2007	Degussa P25 TiO_2 pellet	-	CH_4	0.001(μmol/g-TiO_2/h)	-		top-illuminated quartz cell		311K	4.8W UVC		Tan et al.[151]
										(λ=253.7nm)		
2007	multi-walled carbon nanotube (MWCNT)	-	CH_4, HCOOH, C_2H_5OH	0.98(μmol/g-cat/h)	-		samples laid over glass,	CO_2, H_2O (1:5)	298K	15W UVA		Xia et al.[152]
	TiO_2-MWCNTs(0.01g CNT)	-		11.74	-		stainless steel reactor			(λ=365nm)		
	Degussa P25 TiO_2	-		14.67	-							
	TiO_2-AC(0.01g activated carbon)	-		4.31	-							
	Activated carbons (AC)	-		0.67	-							
2007*	titania-supported cobalt phthalocyanine	0.5wt%CoPc	CO, CH_4, HCOOH, HCHO	0.63(μmol/g-cat/h)	0.21(μmol/g-cat/h)		pyrex cell	CO_2 in $NaOH_{(aq)}$	-	500W halogen lamp		Liu et al.[153]
2007*	$InTaO_4$	-	CH_3OH	-	1.06(μmol/g-cat/h)		continuous flow reactor,	CO_2 in $KHCO_{3(aq)}$		500W halogen lamp		Pan et al.[154]
	NiO-$InTaO_4$	1wt%NiO		-	1.39	2.45% (CH_3OH)	down-window type cell					
2008*	TiO_2(anatase 773K)	-	CH_4	33.68(μmol/g-cat/h)	-		commercial annular reactor	CO_2 in	293-298K	450W Hg lamp		Li et al.[155]
	TiO_2(anatase-rutile 773K)	-		14.03	-			$NaHCO_3$/isopropanol				
	Degussa P25 TiO_2	-		3.51	-							
2008	Degussa P25 TiO_2	-	-	trace	-		optical fiber photoreactor	CO_2, H_2O	348K	UVA light	225mW/cm^2	Nguyen et al.[156]
	Cu-Fe/TiO_2	0.5wt%Cu; 0.5wt%Fe	CH_4, C_2H_4	0.91	-	0.025% (CH_4)				(λ=320-500nm)		
2009	nitrogen-doped titania nanotube (NT)		H_2, CO, CH_4, alkanes,				stainless steel chamber	CO_2, H_2O	317K	sun light (AM 1.5)	75-102mW/cm^2	Varghese et al.[157]
	NT/Pt-460	0.75at%N	olefin, branched paraffin	1.19(μmol/g-cat/h)	-							
	NT/Pt-600	0.4at%N		2.86	-							
	NT/Cu-600	0.4at%N		3.09	-							

	NT/Cu-600	0.4at%N		0.089	-					sun light+ filter (λ>400nm)	78.5mW/cm^2	
				product yield								
year	catalysts	loading	primary products	methane	methanol	quantum yield	reactor/sample cell	reactants	temp.	light source	light intensity	reference
2009*	Degussa P25 TiO_2		CH_3OH	-	430(μmol/g-cat/h)		inner-irradiated quartz cell	CO_2 in $NaOH_{(aq)}$	315K	400W halide lamp		Yang et al.[158]
	TiO_2/SBA-15	45wt%TiO_2		-	972					(λ:300-600nm)		
	Cu/TiO_2	2wt%Cu		-	1250							
	Cu/TiO_2/SBA-15	45wt%TiO_2; 2wt%Cu		-	1444							
2009	Degussa P25 TiO_2 (TO-NP)	-	CH_4	-	-		quartz plate, top-irradiated cell	CO_2, H_2O (50:1)	323K	300W Hg lamp		Zhang et al.[159]
	Pt/TO-NP	0.12wt%Pt		0.06(μmol/g-Ti/h)	-							
	TiO_2 nanotube (TO-NT)	-		-	-							
	Pt/TO-NT	0.15wt%Pt		0.13	-							
2010*	$InTaO_4$(1100°C)	-	CH_3OH	-	0.31(μmol/g-cat/h)		cylindrical quartz reactor	CO_2 in $NaOH_{(aq)}$	298K	fluorescent lamp (λ:452, 543, 611nm)	146mW/cm^2	Wang et al.[127]
	NiO/$InTaO_4$(1100°C)	1wt%Ni		-	2.8	0.0045% (CH_3OH)						
				-	11.1	0.063	optical fiber photoreactor	CO_2, H_2O	298	100W halogen lamp	327mW/cm^2	
				-	21				348	(λ:400-1100nm)		
				-	11.3				305	solar concentrator		
2010	Ga_2SO_3	-	CO	0.72(μmolCO/g-cat/h)	-		quartz reactor	CO_2, H_2O (1:1)		200W Hg/Xe lamp		Tsuneoka et al.[160]
	MgO	-		0.71	-							
	CaO	-		0.35	-							
	ZrO_2	-		0.12	-							
	Al_2O_3	-		0.07	-							
	TiO_2	-	-	-	-							
	V_2O_5	-	-	-	-							
	Nb_2O_5	-	-	-	-							
2010*	TiO_2	-	CH_4, CH_3OH	3.3(μmol/g-cat/h)	0.8(μmol/g-cat/h)		inner-irradiated cell	CO_2 in $NaOH_{(aq)}$		8W Hg lamp (λ=254nm)	1.41mW/cm^2	Koci et al.[161]
	Ag/TiO_2	1wt%		5.2	0.96							
		3		4.2	0.9							
		5		5.6	1.2							
		7		8.5	1.9							
2010	TiO_2-SiO_2	12wt%TiO_2	CO	-	-		continuous flow reactor, side-illuminated cell	CO_2, H_2O		Xe arc lamp	2.4mW/cm^2	Li et al.[162]
	Cu/TiO_2-SiO_2	12wt%TiO_2;0.5wt%Cu	CO, CH_4	13.2(μmol/g-TiO_2/h)	-	0.56% (CH_4)						
2010	Zn2GeO_4(solid-state reaction)	-	CH_4	0.67(μmol/g-cat/h)	-		top-illuminated cell	CO_2, injected H_2O		300W Xe lamp		Liu et al.[163]
	Zn2GeO_4(nanoribbons)	-		1.5	-							
	Pt-loaded nanoribons	1wt%Pt		2	-							
	RuO_2-loaded nanoribbons	1wt%RuO_2		2	-							
	RuO_2+Pt-loaded nanoribbons	1wt%RuO_2;1wt%Pt		25	-							
2010	$ZnGa_2O_4$(solid-state reaction)	-	CH_4	-	-		top-illuminated cell	CO_2, injected H_2O		300W Xe lamp		Yan et al.[164]
	meso-$ZnGa_2O_4$(mesoporous)	-		5.3(ppm/h)	-							
	RuO_2-loaded meso-$ZnGa_2O_4$	1wt%RuO_2		50.4	-							
2010	CdSe quantum dots/Pt/TiO_2	1at%Cd;0.5at%Pt	CO, H_2, CH_4, CH_3OH	48(ppm/g-cat/h) [0.6(μmol/g-cat/h)]	3.3(ppm/g-cat/h)		stainless steel cube	CO_2, H_2O		300W Xe lamp + filter (λ>420nm)	≤100mW/cm^2	Wang et al.[165]

year	catalysts	loading	primary products	product yield: methane	product yield: methanol	quantum yield	reactor/sample cell	reactants	temp.	light source	light intensity	reference
2011	Ti-SBA-15	-	CH_4,C_2H_4,C_2H_6	0.016(μmol/g-cat/h)	-		combinatorial photoreactor	CO_2, H_2O		120 W high-pressure mercury lamp. (280 < λ < 650 nm)	150 mW/cm^2	Yang et al.[125]
2011	TiO_2 (Degussa P25) kaolinite/TiO_2 (KATI66)	99.4wt%TiO_2 60wt%TiO_2	H_2, CH_4, CH_3OH, CO	0.13(μmol/g-TiO_2/h) 0.31	0.03(μmol/gTiO_2/h) 0.18		stirred batch annular reactor	CO_2 in $NaOH_{(aq)}$ (0.2M)		8 W Hg lamps (λ=254 nm)		Kočí et al.[166]
2012	TiO_2 10I–TiO_2 1Cu–TiO_2 0.1Cu–10I–TiO_2 0.5Cu–10I–TiO_2 1Cu–10I–TiO_2 1Cu^{NO3}–10I–TiO_2	- - - - - - - -	CO,CH_4,CH_3Cl	- - 0.109(μmol/g-cat/h) - 0.011 0.011 0.026	- - - - - - -		top-illuminated quartz cell	CO_2, H_2O		450 W Xe lamp (Oriel) (λ > 250 nm)		Zhang et al. [167]
2012	TiO_2-RMA	-	CH_4	2.36(μmol/g-cat/h)	-		glass reactor	CO_2, H_2O		300W mercury lamp (λ=365 nm)		Wang et al. [168]
2013	Pt/$CuGaAlO_4$	- 0.5wt%Pt 1.0wt%Pt 1.5wt%Pt	H_2, CH_3OH, CO	- - - -	- 5.3(μmol/g-cat/h) 7.8 6.1		novel twin reactor divided by a membrane	CO_2, H_2O		300 W xenon (Xe) lamp	90 mW/cm^2	Lee et al.[169]
2013	Mes-TiO2 Mes-CeTi-0.5 Mes-CeTi-1.0 Mes-CeTi-2.0 Mes-CeO2	- - - - -	CH_4, CO	1220(μmol/g-cat/h) 2010 2220 1960 940	- - - - -		stainless steel reactor	CO_2 (95.5%), H_2O (4.5%)	303K	Xe arc lamp (300 W)		Wang et al.[170]

* liquid phase photocatalytic CO_2 reduction. Others: gas phase photocatalytic CO_2 reduction.