

Overview of Ni-based catalysts for hydrogen production from biogas reforming

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Table S1. Influence of promoter on the activity of Ni/Al₂O₃ catalysts for biogas DR.

Promoter (loading, wt%)	Ni loading (wt%)	Preparation method	Reaction conditions			Conversion (%)		Ref.
			CH ₄ /CO ₂ ratio	Temperature (°C)	Time (h)	CH ₄	CO ₂	
-	15	Sol-gel	1	800	37	43.5	50.4	[41]
MgO (37.5)						87.0	90.6	
-	11 (a)	Co-precipitation	1	750	60	40	45	[43]
MgO (10 ^a)						88	92	
-	5	Impregnation	1	700	5	78	n.r.	[47]
MgO (3)						78	n.r.	
-	10	Impregnation	1	550	8.3	39	46	[51]
CeO ₂ (6)						57	69	
CeO ₂ (20)	10	Co-precipitation	1	800	5	75	85	[55]
		Impregnation				52	65	
-	8	Impregnation	1.5	750	20	2	8	[59]
CeO ₂ (10)						30	50	
CeO ₂ (10)-La ₂ O ₃ (4)						50	78	
-	10	Sol-gel	1	800	8	65	75	
CeO ₂ (10)						85	90	[60]
La ₂ O ₃ (10)						70	80	
-	25	Co-precipitation	1	700	5	68	78	
CeO ₂ (5)						60	77	
ZrO ₂ (5)						52	75	[66]
-	8	Impregnation	1.57	800	10	50	80	
La ₂ O ₃ (4)						65	92	
-	15	Impregnation	1	700	36	85	n.r.	
ZrO ₂ (5)						90	n.r.	[72]

n.r.: not reported; (a) mol%

Table S2. Influence of support on the activity of Ni catalysts for biogas DR.

Support	Ni loading (wt%)	Preparation method	Reaction conditions			Conversion (%)		Ref.
			CH ₄ /CO ₂ ratio	Temperature (°C)	Time (h)	CH ₄	CO ₂	
Al ₂ O ₃	8	Impregnation	1	750	30	52	60	[39]
MgO-Al ₂ O ₃					100	88	90	
MgO					100	75	80	
Al ₂ O ₃	10	Impregnation	1	750	2 (a)	80	n.r	[40]
MgO					12	64		
CeO ₂						50		
CeO ₂	5	Impregnation	1	500	10	30	44	[52]
Al ₂ O ₃	10	EISA (b)	1	800	72	50	65	[57]
CeO ₂ -Al ₂ O ₃						70	80	
CeO ₂	5	Impregnation	1	700	5	68	70	[75]
Ce _{0.6} Zr _{0.4} O ₂						62	n.r.	
ZrO ₂	5	Impregnation	1	600	24	48	62	[77]
CeO ₂						15	21	
Ce _{0.6} Zr _{0.4} O ₂						28	50	
ZrO ₂ (amorphous)	5	Impregnation	1	750	50	92	98	[79]
ZrO ₂ (monoclinic)						35 (c)	42 (c)	
ZrO ₂	8	Impregnation	1.5	750	28	22	45	[83]
La ₂ O ₃ -ZrO ₂						40	58	
CeO ₂ -ZrO ₂						42	62	
Al ₂ O ₃	5	Impregnation	1	700	9	77	75	[85]
HY						61	63	
HZSM-5						75	79	
SiO ₂	10	Impregnation	1	800	9	40	55	[94]
MCM-41						65	75	

n.r.: not reported; (a) the reactor was blocked; (b) EISA: evaporation-induced self-assembly; (c) severe deactivation

Table S3. Influence of transition metals on the activity of Ni bimetallic catalysts for biogas DR.

Metal (loading, wt%)	Support	Ni loading (wt%)	Preparation method	Reaction conditions			Conversion (%)		Ref.
				CH ₄ /CO ₂ ratio	Temperature (°C)	Time (h)	CH ₄	CO ₂	
- Co (0.89)	H-ZrO ₂	4.82 3.83	Co-impregnation	1	700	80	51 69.1	60 75.7	[113]
- Co (2.5)	Al ₂ O ₃	10 7.5	Co-impregnation	1	600	24	23 30	n.r.	[116]
- Co (2.5)	Al ₂ O ₃	5	Co-impregnation with templating agent	1	700	97	69 73.1	76 81.6	[117]
- Cu (2.81)	Mg(Al)O	12 8.96	Co-precipitation	1	600	25	43 51	56 58	[128]
- Cu (0.83)	Al ₂ O ₃	7.5 10	Co-impregnation	1	750	7	82 92	85 94	[129]
- Cu (1.0)	Al ₂ O ₃	10	Co-impregnation	1	750	16	64 92	n.r.	[130]
- Cu (0.5)	SiO ₂	4	Electrostatic adsorption	1	750	16 50	22 78	51 85	[131]
Fe (2.49)	Al ₂ O ₃	7.25	EISA (a)	1	600	50	19	30	[135]
Fe (5.03)		4.98					28	40	
- Fe (4.2)	Al ₂ O ₃	15.7 9.6	Modified EISA (a)	1	450	20	8 10	10 14	[136]

n.r.: not reported; (a) EISA: evaporation-induced self-assembly

Table S4. Influence of noble metals on the activity of Ni bimetallic catalysts for biogas DR.

Metal (loading, wt%)	Support	Ni loading (wt%)	Preparation method	Reaction conditions			Conversion (%)		Ref.
				CH ₄ /CO ₂ ratio	Temperature (°C)	Time (h)	CH ₄	CO ₂	
- Pt (0.4)	Al ₂ O ₃	10	Reverse microemulsion	1	700	14	n.r.	58 71	[139]
- Pt (0.5)	ZSM-5	5.0 5.5	Sequential impregnation	1	600	2	20.7 28.4	58.1 65	[141]
- Pt (0.54)	silicalite-1 zeolite	1.96 1.58	Impregnation	1	800	6	65 70	74 80	[142]
- Pt (0.4)	Al ₂ O ₃	10	Impregnation	1	700	14	n.r.	50 69	[144]
- Rh (1.75)	Al ₂ O ₃	10	Impregnation	1	800	4	62 70	68.4 76	[27]
- Rh (0.6)	MgAl ₂ O ₄	2.2 1.6	One-pot sol-gel	1	600	20	36 42	45 52	[147]
- Rh (3.75)	SiO ₂	5 1.25	Impregnation	1	700	24	72 83	77 84	[148]
- Rh (1.0) Pd (0.5)	CeO ₂ -Al ₂ O ₃	15 14 14.5	Impregnation	1	700	48	57.7 68.3 51.9	72.4 81.4 66.9	[149]
- Pd (1.3)	ZrO ₂ -La ₂ O ₃	5 5.4	Impregnation	1	700	2	49 73	62 78	[150]
- Pd (0.5)	Al ₂ O ₃	6	Co-impregnation	1	750	100	75 85	82 92	[151]
- Pd (0.2)	MgO	5	Deposited by sublimation	1	750	100 200	94.4 96.5	96.1 95.5	[152]
- Ru (0.6)	Al ₂ O ₃	11.6 13.1	Impregnation	1	800	11	10 37	17 48	[155]

n.r.: not reported;

Table S4. Continued.

Metal (loading, wt%)	Support	Ni loading (wt%)	Preparation method	Reaction conditions			Conversion (%)		Ref.
				CH ₄ /CO ₂ ratio	Temperature (°C)	Time (h)	CH ₄	CO ₂	
- Ru (0.7)	MgO – CR (a)	9.6 9.2	Solvothermal	1	800	100	83 87	89 94	[156]
- Ru (0.7)	MgO – DR (b)	9.6 9.2	Solvothermal	1	800	100	81 78	89 86	[156]
- Ru (0.66)	Al ₂ O ₃	8 8.2	Impregnation	1	800	2	95 100	85 71	[157]
- Ru (0.75)	SiO ₂	6 6.9	Impregnation	1	800	2	37 61	50 62	[157]
- Ru (0.35)	MgO-Al ₂ O ₃	17.2 15.2	Impregnation	1	650	2	55 28	66 39	[158]

n.r.: not reported; (a) CR: calcination with subsequent reduction; (b) DR: direct reduction