

Electronic Supplementary Material

Placing Ni(II) ions in various positions in/on layered double hydroxides – synthesis, characterization and testing in C–C coupling reactions

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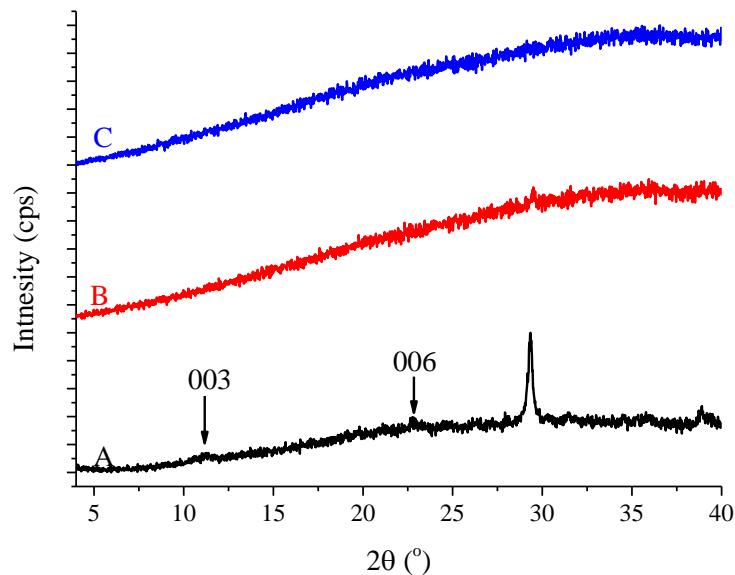
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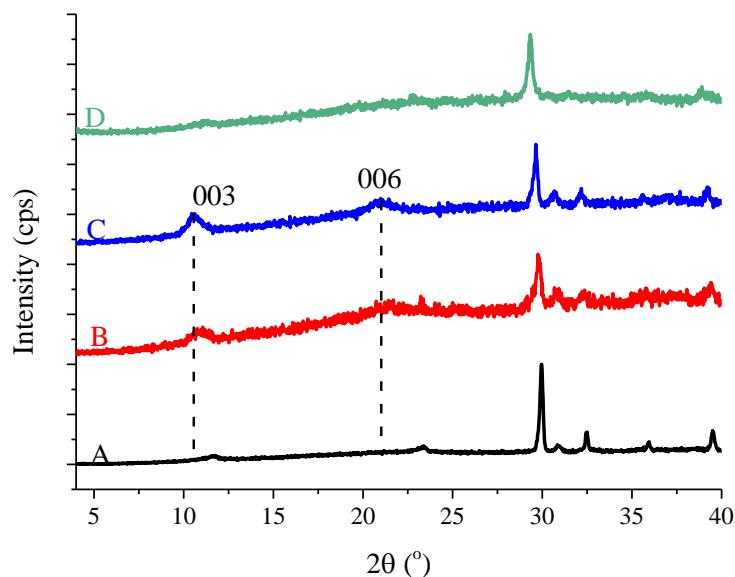
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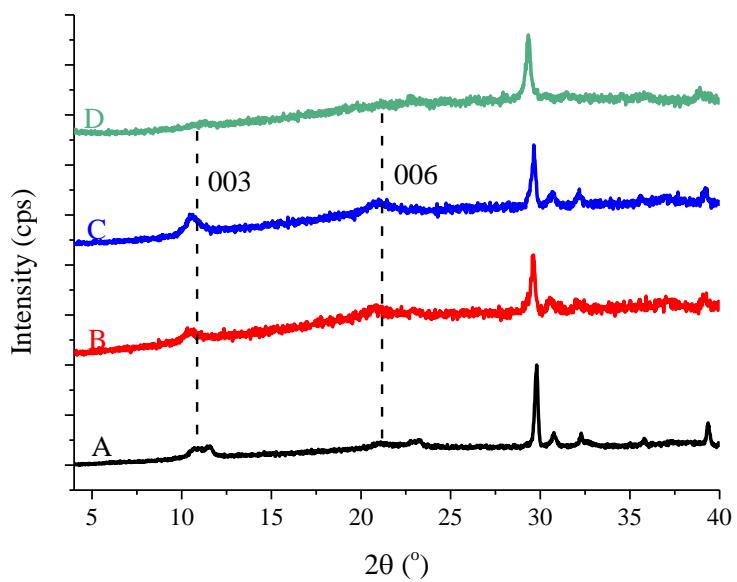
1 Optimization of the LDH synthesis procedure on the example of the Ni(II)Ca(II)Fe(III)-LDH



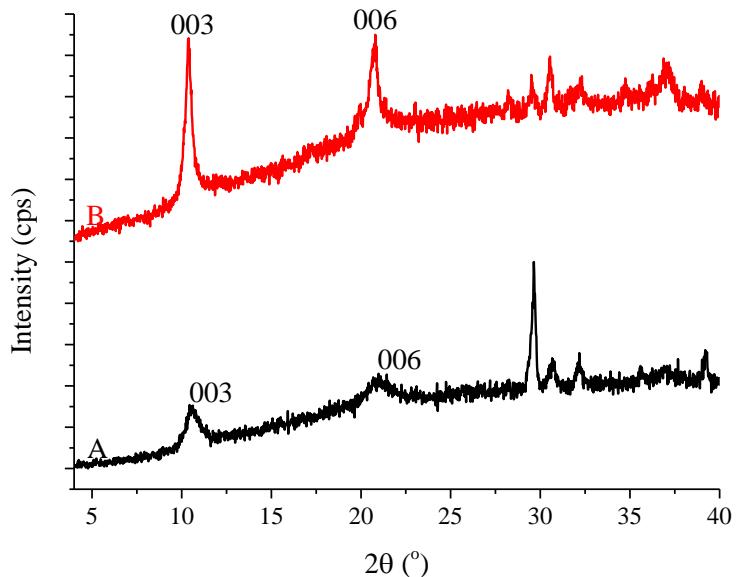
SFig. 1 X-ray diffractograms concerning Ni(II)Ca(II)Fe(III)-LDH. Dependence on the pH. A: pH = 10.5, B: pH = 9.5, C: pH = 8.5 (Ni(II):Ca(II) = 1:1, T = 35 °C)



SFig. 2 X-ray diffractograms concerning Ni(II)Ca(II)Fe(III)-LDH. Dependence on the ratio of bivalent cations. A: 0.1:1.9, B: 0.5:1.5, C: 0.75:1.25, D: 1:1 (pH = 10.5, T = 35°C)

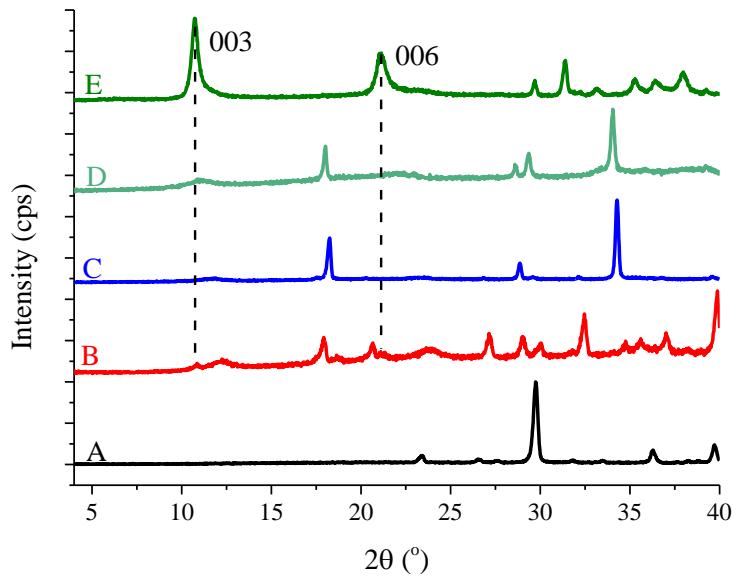


SFig. 3 X-ray diffractograms concerning Ni(II)Ca(II)Fe(III)-LDH. Dependence on the temperature. A: T = 25°C, B: T = 35°C, C: T = 45°C, D: T = 55 °C (pH = 10.5, Ni(II):Ca(II)= 0.75:1.25)

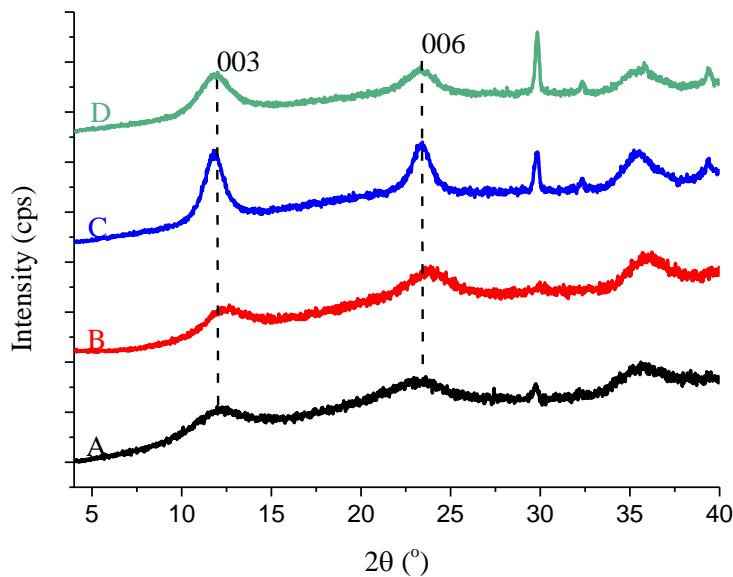


SFig. 4 X-ray diffractograms concerning Ni(II)Ca(II)Fe(III)-LDH. Dependence on the post-treatment time. A: 8 h, B: 24 h (pH = 10.5, Ni(II):Ca(II)= 0.75:1.25, T = 45 °C)

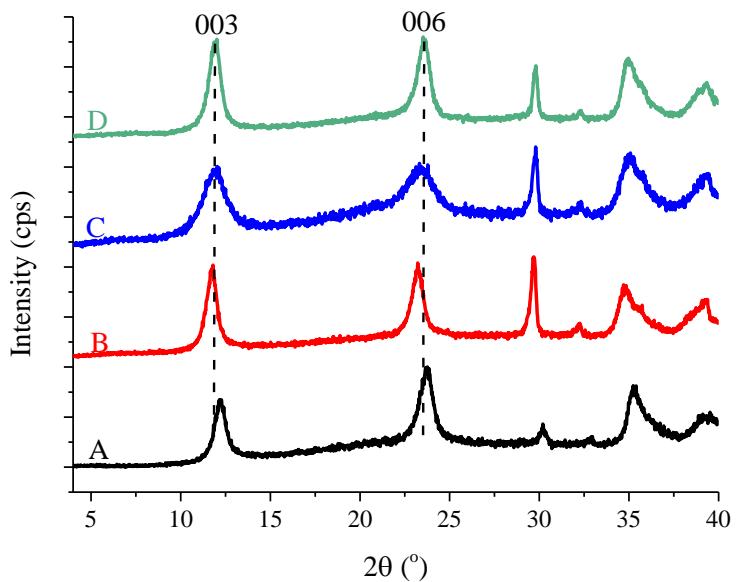
2 The crucial experimental factors for the development of the other LDHs



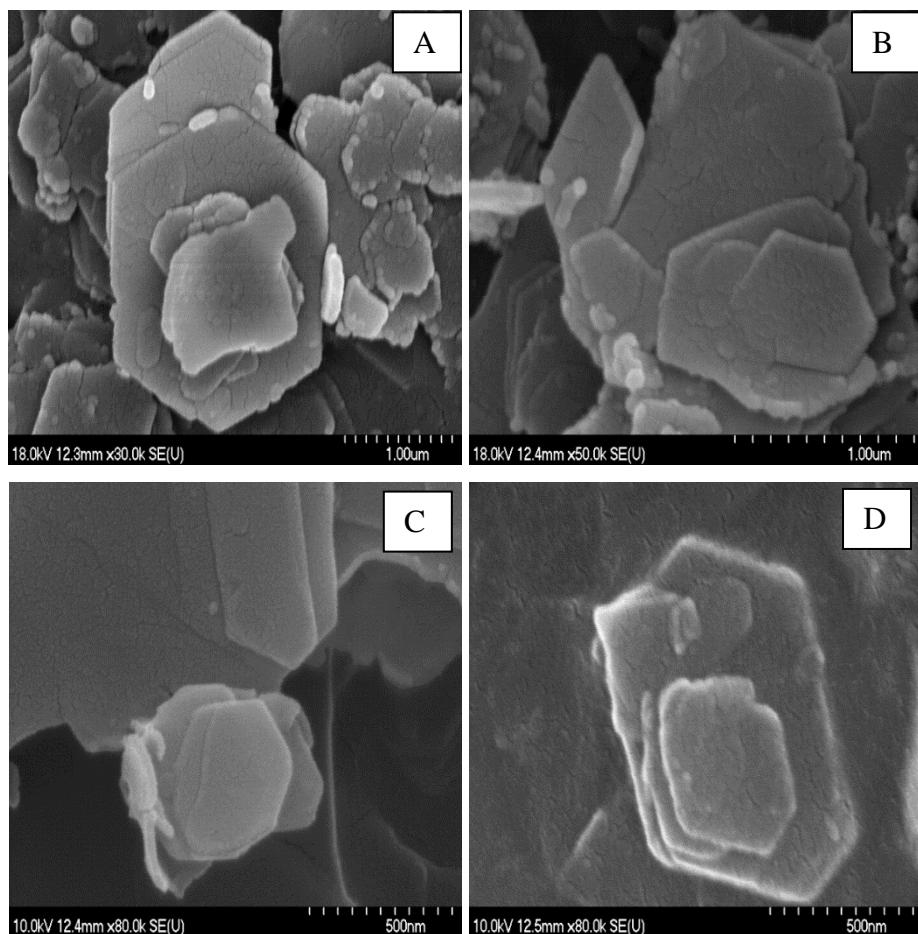
SFig. 5 X-ray diffractograms for the development of the Ni(II)Ca(II)Al(III)-LDH; A: pH= 7.0, B: pH = 8.0, C: pH = 9.0, D: pH = 10.0, E: pH = 11.0 (Ni(II):Ca(II)= 0.1:1.9, T= 45 °C)



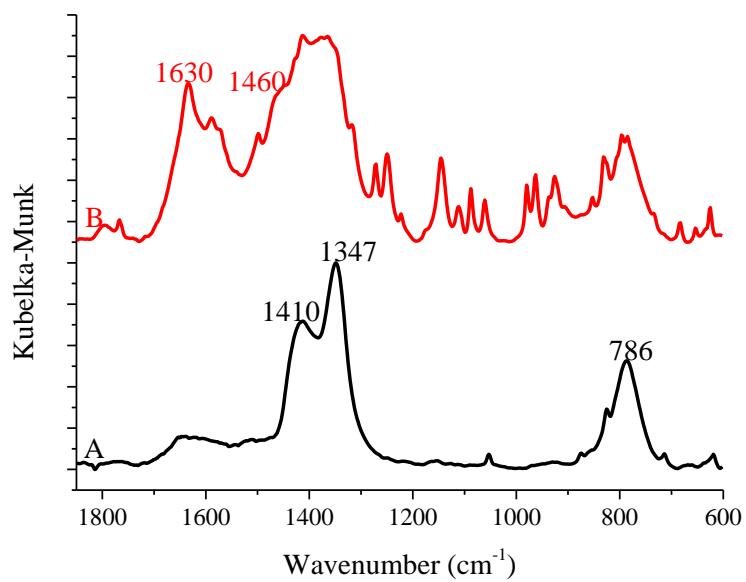
SFig. 6 X-ray diffractograms of the NiAl-LDH samples. Dependence on the ratio of cations. A: 1:1, B: 2:1, C: 3:1, D: 4:1 (T = 25 °C, pH = 9.5)



SFig. 7 X-ray diffractograms of the Ni(II)Mg(II)Al(III)-LDH samples. Dependence on the ratio of bivalent cations. A: 0.1:1.9, B: 0.5:1.5, C: 0.75:1.25, D: 1:1 (pH = 10.5, T = 45 °C)



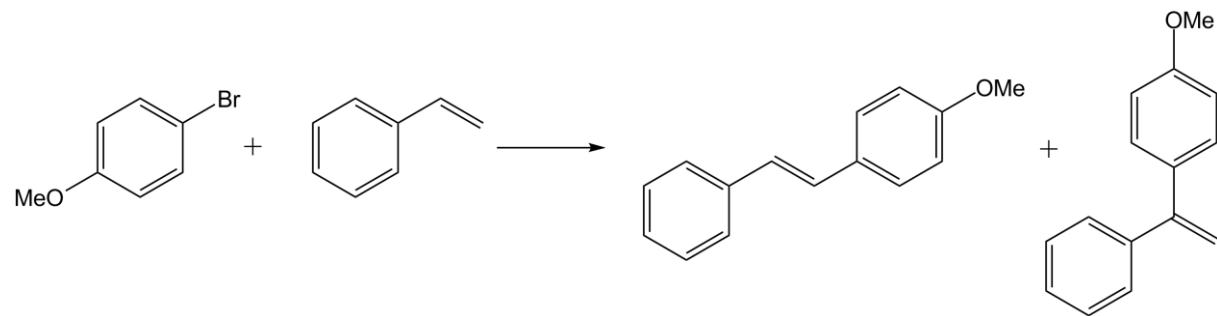
SFig. 8 SEM images of the successfully precipitated multicomponent LDH and the NiAl-LDH samples. A: Ni(II)Ca(II)Fe(III)-LDH, B: Ni(II)Ca(II)Al(III)-LDH, C: Ni(II)Mg(II)Al(III)-LDH, D: Ni(II)Al(III)-LDH



SFig. 9 The IR spectra of A: CaAl-LDH and B: Ni(II)-cysteinate–Ca₂Al-LDH

3 Optimization of the catalytic reactions

3.1 The Heck reaction



SScheme 1 Heck reaction between 4-bromoanisole and styrene

STable 1 Optimization of the reaction conditions for the Heck reaction. Dependence on the amount of catalyst [5 cm³ of DMF, 251 µl of 4-bromoanisole (2.0×10^{-3} mol), 275 µl of styrene (2.4×10^{-3} mol), 120 h reaction time at 323 K]

LDH samples	Conversion (%)			
	5 mg	15 mg	30 mg	60 mg
Ni _{0.1} Ca _{1.9} Al	6	19	36	44
Ni _{0.1} Mg _{1.9} Al	5	15	33	37
Ni _{0.75} Ca _{1.25} Fe	20	54	56	61
Ni ₂ Al	34	37	44	49
NiO-doped Ca ₂ Al	35	45	47	51
Ni(II)-cysteinate–Ca ₂ Al	3	10	22	28

STable 2 Optimization of the reaction conditions for the Heck reaction. Dependence on the solvents (5 mg of NiO-doped and NiAl-LDH/15 mg of NiCaFe-LDH/30 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 5 cm³ of solvents, 251 µl of 4-bromoanisole (2.0×10^{-3} mol), 275 µl of styrene (2.4×10^{-3} mol) 120 h reaction time at 323 K)

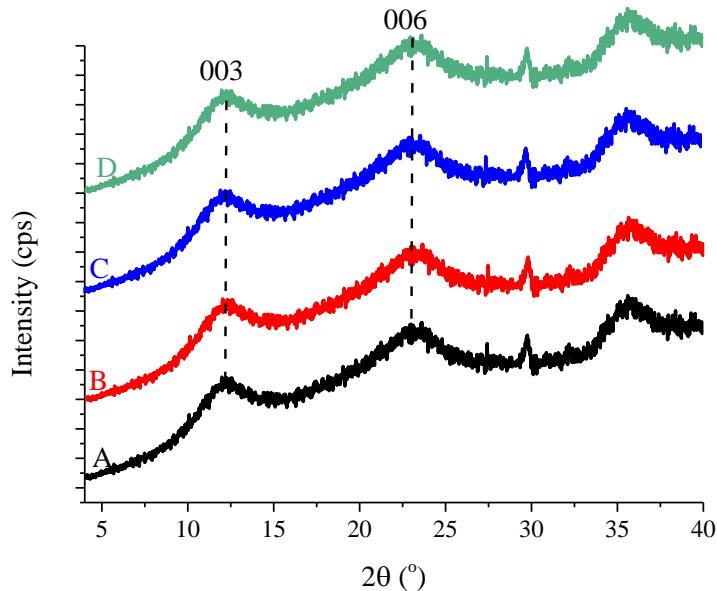
LDH samples	Conversion (%)						
	DMF	DMSO	water	toluene	water/toluene 50/50	water/toluene 85/15	ethanol
Ni _{0.1} Ca _{1.9} Al	36	34	9	20	28	8	8
Ni _{0.1} Mg _{1.9} Al	33	30	4	17	25	—	9
Ni _{0.75} Ca _{1.25} Fe	54	41	7	30	40	10	—
Ni ₂ Al	34	29	—	12	21	5	5
NiO-doped	35	29	6	17	27	—	—
Ni(II)-Cys	22	19	—	5	13	3	9

STable 3 Optimization of the reaction conditions of Heck reaction: dependence of the applied base (5 mg of NiO-doped and NiAl-LDH/15 mg of NiCaFe-LDH/30 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 5 cm³ of water:toluene 50/50% mixture, 251 µl of 4-bromoanisole (2.0×10^{-3} mol), 275 µl of styrene (2.4×10^{-3} mol), applied base (2.8×10^{-3} mol) 120 h reaction time at 323 K)

LDH samples	—	Conversion (%)						
		K ₂ CO ₃	KOAc	Na ₂ CO ₃	Pyr	Piper	NaOAc	Al ₂ O ₃
Ni _{0.1} Ca _{1.9} Al	28	50	57	47	39	33	—	—
Ni _{0.1} Mg _{1.9} Al	25	46	51	42	33	27	—	—
Ni _{0.75} Ca _{1.25} Fe	40	70	79	63	48	40	—	—
Ni ₂ Al	21	32	31	30	25	25	—	—
NiO-doped	27	55	62	50	35	31	—	—
Ni(II)-Cys	13	41	46	35	20	17	—	—

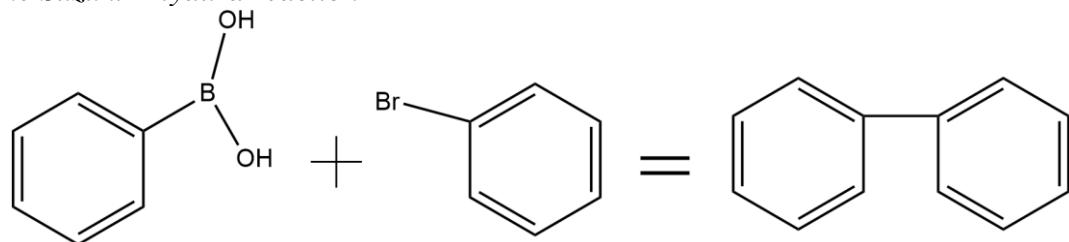
STable 4 Optimization of the reaction conditions for the Heck reaction. Dependence on the temperature [5 mg of NiO-doped or NiAl-LDH/15 mg of NiCaFe-LDH/30 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 5 cm³ of water:toluene 50/50% mixture, 251 µl of 4-bromoanisole (2.0×10^{-3} mol), 275 µl of styrene (2.4×10^{-3} mol), 275 mg of KOAc as base (2.8×10^{-3} mol), 120 h reaction time]

LDH samples	Conversion (%)		
	298 K	323 K	348 K
Ni _{0.1} Ca _{1.9} Al	15	57	65
Ni _{0.1} Mg _{1.9} Al	20	51	59
Ni _{0.75} Ca _{1.25} Fe	30	79	83
Ni ₂ Al	9	31	40
NiO-doped Ca ₂ Al(II)	23	62	69
Ni(II)-Cys–Ca ₂ Al	8	46	50



SFig. 10 X-ray diffratograms of NiAl-LDH samples used in the Heck reaction. After A: the reaction, B: the 1st recycling, C: the 2nd recycling and D: the 3rd recycling

3.2 The Suzuki-Miyaura reaction



SScheme 2 The Suzuki-Miyaura reaction between phenylboronic acid and bromobenzene.

STable 5 Optimization of the reaction conditions for the Suzuki-Miyaura reaction. Dependence on the amounts of the catalysts (3.5 cm³ of DMF, 105 µl of bromobenzene (1.0×10^{-3} mol), 146 mg of phenylboronic acid (1.2×10^{-3} mol), 120 h reaction time at 298 K)

LDH samples	Conversion %			
	5 mg	15 mg	25 mg	50 mg
Ni _{0.1} Ca _{1.9} Al	7	20	33	4
Ni _{0.1} Mg _{1.9} Al	6	19	30	34
Ni _{0.75} Ca _{1.25} Fe	13	41	50	55
Ni ₂ Al	30	37	44	48
NiO-doped Ca ₂ Al	44	51	54	59
Ni(II)-Cys-Ca ₂ Al	8	22	32	40

STable 6 Optimization of the reaction conditions for the Suzuki-Miyaura reaction. Dependence of the solvents (5 mg of NiO-doped and NiAl-LDH/15 mg of NiCaFe-LDH/25 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 3.5 cm³ of solvents, 105 µl of bromobenzene (1.0×10^{-3} mol), 146 mg of phenylboronic acid (1.2×10^{-3} mol), 120 h reaction time at 298 K)

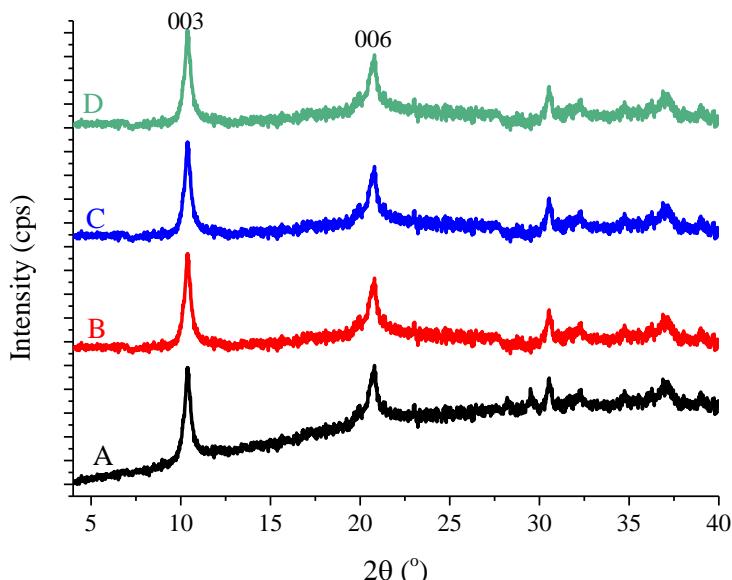
LDH samples	Conversion (%)						
	DMF	DMSO	water	toluene	water/toluene 50/50	water/toluene 85/15	ethanol
Ni _{0.1} Ca _{1.9} Al	33	29	—	14	9	17	—
Ni _{0.1} Mg _{1.9} Al	30	26	—	7	10	18	—
Ni _{0.75} Ca _{1.25} Fe	41	36	—	17	13	22	—
Ni ₂ Al	30	25	—	10	6	15	—
NiO-doped	44	36	—	13	14	23	—
Ni(II)-Cys	32	22	—	9	11	16	—

STable 7 Optimization of the reaction conditions for the Suzuki-Miyaura reaction. Dependence on the applied base [5 mg of NiO-doped and NiAl-LDH/15 mg of NiCaFe-LDH/25 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 3.5 cm³ of water:toluene 85/15% mixture, 105 µl of bromobenzene (1.0×10^{-3} mol), 146 mg of phenylboronic acid (1.2×10^{-3} mol), applied base (2.5×10^{-3} mol), 120 h reaction time at 298 K].

LDH samples	Conversion %							
	—	K ₂ CO ₃	KOAc	Na ₂ CO ₃	Pyr	Piper	NaOAc	Al ₂ O ₃
Ni _{0.1} Ca _{1.9} Al	17	—	7	5	23	33	—	—
Ni _{0.1} Mg _{1.9} Al	18	—	11	11	24	34	—	—
Ni _{0.75} Ca _{1.25} Fe	22	—	12	13	29	38	—	—
Ni ₂ Al	15	—	12	9	20	29	—	—
NiO-doped	23	—	12	12	26	36	—	—
Ni(II)-Cys	10	—	10	7	19	29	—	—

STable 8 Optimization of the reaction conditions for the Suzuki-Miyaura reaction. Dependence on the temperature [5 mg of NiO-doped and NiAl-LDH/15 mg of NiCaFe-LDH/25 mg of intercalated system and NiCaAl-LDH and NiMgAl-LDH, 3.5 cm³ of water:toluene 85/15% mixture, 105 μ l of bromobenzene (1.0×10^{-3} mol), 146 mg of phenylboronic acid (1.2×10^{-3} mol), 246 μ l of piperidine as base (2.5×10^{-3} mol), 120 h reaction time].

Composites	Conversion (%)		
	298 K	323 K	348 K
Ni _{0.1} Ca _{1.9} Al	33	49	55
Ni _{0.1} Mg _{1.9} Al	34	43	44
Ni _{0.75} Ca _{1.25} Fe	38	60	66
Ni ₂ Al	29	35	37
NiO-doped Ca ₂ Al	36	57	64
Ni(II)-Cys-Ca ₂ Al	29	34	37



SFig. 11 X-ray diffratograms of NiCaAl-LDH used in the Suzuki-Miyaura reaction. A: the original, after B: the reaction, C: the 1st recycling and D: the 2nd recycling