ESI

CATALYSIS IN PICKERING EMULSIONS

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Table S1. Summary of published literature involving catalysis in various kinds of Pickering emulsions.

Ref.	Liquid 1	Liquid 2	Particle emulsifier (size)	Catalyst	Emulsion type	Chemical reaction	Comments
25	Water	Isooctane	SiO_2 nanoparticles hydrophobised *in situ* by *N*,*N*-dimethyldodecylamine (20 nm)	Lipase from *Candida rugosa*	o/w	Hydrolysis of olive oil and esterification of octanol with oleic acid	Destabilisation/re-emulsification by bubbling N_2 and CO_2, respectively
26	Water	Heptane	CALB[a] immobilised on polymeric nanoparticles prepared by copolymerization of styrene and glycidyl methacrylate (228 nm)		o/w	Esterification of hexanol with hexanoic acid	HIPE[b]
60	Water	Decane	Mesoporous and non-porous SiO_2 modified with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride or octadecyl trimethoxysilane (~100 nm)	Rh-TPPTS[c]	o/w	Hydroformylation of 1-octene	-
68	Water	1-Dodecene	Hydrophilic SiO_2 (l = 100 nm, d = 20 nm) or hollow Halloysite[d] nanotubes (l = 800 nm, d = 50 nm)	Rh-sulfonated 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene	o/w	Hydroformylation of 1-dodecene	-
75	Water	Toluene	Pd/triamine-octyl bifunctionalized hairy		o/w	Hydrogenation of	Protonation/deprotonati

			SiO_2 (250-350 nm)			styrene	on switches the wettability of the catalyst surface thus driving emulsion inversion (o/w to w/o)
76	Water	1-Methylnaphthalene	TiO_2 (14 nm)		o/w	Photocatalytic degradation of 1-methylnaphthalene	Photocatalytic degradation with UV light
78	Water	Styrene	Pd (2-6 nm)/graphitic carbon nitride sheets (g-C_3N_4)		o/w	Hydrogenation of alkenes	H_2 generated *in situ* from NH_3BH_3
79	Water	Toluene	Amino-functionalised TiO_2 (l = 20-45 nm, d = 10-15 nm)		o/w	Hydrogenation of styrene	Destabilisation/re-emulsification by addition of HCl and NaOH, respectively
81	Water	Hexadecane	Cellulose nanofibers with aldehyde groups (ACNFs) (l. ~20 nm)	Pd, Pt and Au	o/w	Reduction of 4-nitrophenol and common dyes (methylene blue and methyl orange) with $NaBH_4$	Nanoparticles are grown *in situ* on interfacial ACNFs layer through aldehyde induced reduction of $[PdCl_4]^{2-}$, $[AuCl_4]^-$ or $[PtCl_6]^{2-}$. Continuous flow reaction
86	Water	Decalin	Pd/Janus nanoparticles (silica functionalised with aminopropyltriethoxysilane, APTES) (~ 20 nm)		o/w	Hydrogenation of benzaldehyde and glutaraldehyde	Phase-selective catalysis
104	Water	Toluene	HDPA[e]-functionalized Fe_2O_3-MO_x)/Al_2O_3 nanoparticles (M is either Mn, Co, Ni, Cu, Cr, Mo, V or Ti) (~ 80 nm)		o/w	Oxidation of toluene to benzaldehyde	-
87	Water	Bio-octanol	TiO_2 particles modified with 3-		o/w	Photocatalytic H_2	Reaction triggered with

			(trimethoxysilyl)propyl methacrylate (1.8 μm)			production	light
98	Water	Hexane	8A PEG-CD[f] and 8A PEG-Fc[g] self-assembled into stimulated microgels (~ 200 nm)	Lipase from *Pseudomonas cepacia*	o/w	Hydrolysis of triacetin and kinetic resolution of (*R*,*S*)-1-phenylethanol	Fc is redox-active and the electrochemical response allows the reversible formation and deformation of the microgels which affects emulsion stability
108	Water	Heptane	Lipase from *Candida rugose* chemically conjugated to polydopamine-modified ZIF-8[h] particles (50, 150 and 500 nm)		o/w	Hydrolysis of *p*-nitrophenyl palmitate	-
112	Water	Toluene	Bare, metal-functionalised and magnetic-functionalised porous hollow carbonaceous spheres synthesized from *S. Cerevisiae* cells (2 μm)	Sodium sulphide, $NaBH_4$	o/w	Reduction of *p*-nitroanisole	Destabilisation/re-emulsification is pH- and magnetic field-dependent
113	Water	Decanol	Au/PEO[i]-b-P4VP[j] hybrid micelles (56 nm)		o/w	Reduction of *p*-nitroanisole to *p*-anisidine	Destabilisation/re-emulsification by addition of HCl and NaOH, respectively
80	Water	Various aliphatic hydrocarbons	MgO (300-400 nm or 1300-2900 nm)		o/w	Knoevenagel condensation reaction	Emulsion stability and catalytic activity of MgO were affected by method of preparation, calcination temp. and

							nature of oil
88	Water	Various	Cellulose nanocrystals partially modified with alkyl chains (Janus particles) decorated with Pd (~ 1 µm)		o/w	Hydrogenation of nitrobenzene and Suzuki coupling	-
105	Water	Bromooctane	Graphene oxide grafted with polyethylene glycol (PEG) and 3-aminopropyltriethoxysilane (APS)		o/w	Production of iodooctane from bromooctane and NaI (nucleophilic substitutions)	-
20	Water	Decalin	Pd/carbon nanotube-inorganic oxide hybrid nanoparticles (~100 nm)		w/o	Hydrodeoxygenation of a phenolic compound and hydrogenation and etherification of an aldehyde	Consecutive reaction: sequence of Pd-catalysed hydrogenation paired with a preceding aldol condensation
15	Phosphate buffer	Hexane	Partially hydrophobic SiO_2 modified with methyltrimethoxysilane (40-60 nm)	CALB[a]	w/o	Hydrolysis kinetic resolution of racemic esters	-
22	Phosphate buffer	Toluene	Hydrophobic SiO_2 nanoparticles (50, 120 and 230 nm) and mesoporous silica particles (120 nm)	Lipase from *Candida sp.*	w/o	Esterification reaction between 1-hexanol and hexanoic acid	Cross-linking of particles at droplet interface with TEOS[k]
49	Phosphate buffer	Paraffin oil	Lipase from *Pseudomonas cepacia* immobilized on mesoporous SiO_2 (350-450 nm) modified with silylating agents of different chain lengths		w/o	Tributyrin hydrolysis	Emulsion prepared with particles of intermediate wettability displayed highest stability and conversion
54	Water	Cyclopentyl methyl ether,	SiO_2 (20 nm)	CALA[l]	w/o	Transesterification of 1-phenyl ethanol	Continuous flow reaction

		methyl tert-butyl ether or toluene				with vinyl butyrate	
55	Water	Toluene	Partially hydrophobic SiO_2 modified with methyltrimethoxysilane (40-60 nm)	Various: H_2SO_4, HPA[m] and CALB[a]	w/o	Addition reaction, ring opening of an epoxide, kinetic resolution of racemic esters	Continuous flow reaction
56	Water	Heptane or methyl tert-butyl ether	SiO_2 hydrophobized with TMODS[n] (140 nm)	CALA,[l] CALB[a] and benzaldehyde lyase from *Pseudomonas fluorescens* Boivar I	w/o	Esterification of 1-octanol and octanoic acid and stereoselective condensation of benzoins	-
57	Water	Heptane or dodecane	Fe_3O_4 on SiO_2 (~220 nm)	Lipase from *Candida sp*. expressed in *Aspergillus niger*	w/o	Esterification of 1-hexanol with hexanoic acid	-
58	Water	Toluene	Polymersomes (200-500 nm) Polymersomes containing CALB[a] (200-500 nm)	CALB[a]	w/o	Esterification of 1-hexanol and hexanoic acid	-
59	Phosphate buffer	Toluene	Lipase from *Candida sp*. immobilized onto periodic mesoporous organosilica (1.5 μm)		w/o	Esterification of oleic acid with ethanol	-
61	Phosphate buffer	Hexane	Mesoporous SiO_2 containing either lysozyme or lipase from *Pseudomonas cepacia* (2-6 μm)		w/o	Hydrolysis of triacetin and kinetic resolution of (*R*,*S*)-1-phenylethanol with vinyl acetate	Recyclability is not ideal as activity decreases after each cycle
62	Phosphate	Cyclohexane	CALB[a] immobilised on SiO_2		w/o	Esterification and	-

	buffer		nanoflowers modified with DCDMS[o] (500 nm)			transesterification for biodiesel production	
63	Water	Decalin	Zeolite modified with OTS[p] (~500 nm)		w/o	Alkylation of *m*-cresol with 2-propanol	-
65	Water	Toluene	Partially hydrophobic SiO_2 (40-60 nm)	$H_3PW_{12}O_{40}$ (HPA[m])	w/o	Cyclization of citronellal	Continuous flow reaction
66	Water	Toluene	Partially hydrophobic SiO_2 modified with methyltrimethoxysilane (130-200 nm)	HCl and $NaBH_4$	w/o	Deacetalization-reduction, deacetalization − Knoevenagel, deacetalization−Henry and diazotization−iodization cascade reactions	Cascade reactions
67	H_2SO_4 and EDA[q] in water	Toluene	SiO_2 modified with methyltrimethoxysilane (60-80 nm)	H_2SO_4, EDA[q]	w/o	Deacetalization-Knoevenagel cascade reaction	Sol-gel process with TMOS[r] to reinforce droplets
69	Water	Ethyl acetate	Pd on SiO_2 modified with $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$ and $(MeO)_3Si(CH_2)_7CH_3$ (50-60 nm)		w/o	Hydrogenation of unsaturated compounds	Destabilisation/re-emulsification by addition of HCl and NaOH, respectively
71	Water	Decalin	Pd/Al_2O_3 coated with organophosphonic acids of various alkyl chain lengths (size not given)		w/o	Vanillin hydrodeoxygenation	-

72	Water	Cinnamaldehyde	Pd(8-10 nm)/silicane-functionalised graphene oxide (size not given)	w/o	Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde	-
73	Water	Toluene	$[C_{18}/SO_3H]@SiO_2$ (15 nm) and $[C_{12}]_3[PW_{12}O_{40}]^s$ (35 nm) mixtures	w/o	Oxidative cleavage of cyclohexene oxide for synthesis of adipic acid	One-pot reaction. Other cycloalkene oxides, nanoparticles and organic solvents also tested
74	Water	Decalin	Rh/carbon nanotubes (l = 1-2 µm, d = 10-20 nm)	w/o	Hydrodeoxygenation of vanillin	-
16	Water	Toluene	Pd/triamine-octyl-bifunctionalized SiO_2 (250-350 nm)	w/o	Reduction of *m*-nitrotoluene	-
77	Water	Toluene	Pd loaded onto carbon spheres (160 nm)	w/o	Hydrogenation of unsaturated aromatic compounds	-
90	Tris-HCl buffer	Hexane	Lipase-immobilized alginate microparticles coated with silanized TiO_2 nanoparticles (2-5 µm)	w/o	Esterification of hexanoic acid and 1-hexanol	Microparticles prepared through alginate gelation *via* coalescence of two w/o emulsions
83	Water	Isooctane	Multi-walled carbon nanotubes (w. ~200 nm), graphene and Ag_3PO_4 (~ 80 nm)/$BiPO_4$ (l. ~200 nm, d. ~80 nm) composites	w/o	Photocatalytic degradation of Blue 92 dye	-
99	Triethanolamine hydrochloride buffer	Methyl-*tert*-butyl ether	Negatively charged P(NiPAM-*co*-MAA)^t microgel, copolymer / Alcohol dehydrogenase from *Lactobacillus brevis*	w/o	Reduction of acetophenone to (*R*)-phenylethanol	Destabilisation by increasing temperature above VPTT^v of microgel. The coupled reaction of 2-propanol

			P(NiPAM-*co*-NiPMAM)[u] microgel and PNiPAM-PNiPMAM core–shell microgel (200 nm in swollen state)				to acetone is used to regenerate the co-factor NADPH
100	Water	Toluene	SiO_2 (~ 10 nm) and PDEAEMA[w] microgel containing lipase from *Candida sp*. expressed in *Aspergillus niger* (1-2 µm)		w/o	Esterification of 1-hexanol with hexanoic acid	pH change induces swelling/shrinking of microgel
116	Water	Decalin	Metal (Pd, Pt, Ni) oxides fused to functionalized carbon nanotubes (l. ~ 100 nm)		w/o	Simultaneous condensation and hydrogenation of short biomass-derived oxygenates	Multi-step reaction
30	Water	Toluene	Titanate nanotubes modified with $CH_3Si(OCH_3)_3$ (l. 100 – 400 nm, w. 4 – 7 nm)	Titanate nanotubes containing Ru nanoparticles (2 – 3 nm) in the interior of the hollow tubular structure	w/o	Selective hydrogenation of α,β-unsaturated aldehydes	-
21	$ZnSO_4 \cdot 7H_2O$ in water	Benzene	TiO_2 nanoparticles modified with $(MeO)_3SiCH_3$ (21 nm)	Ru/TiO_2	o/w and w/o	Selective hydrogenation of benzene to cyclohexene	Impact of emulsion type, droplet diameter, inter-droplet distance and temperature
29	Phosphate buffer	Dodecane	SiO_2 particles of various hydrophilicities (20 nm)	Aldoxime dehydratase (OxdB)	o/w and w/o	Dehydration of *n*-octanaloxime	Compared reaction rate and extent in both emulsion types

				overexpressed in *E. coli*				
50	Water	Decalin	Pd/carbonaceous microspheres (1.5-2.5 μm)		o/w or w/o	Hydrodeoxygenation of vanillin	-
107	Water	Cyclopentyl methyl ether	P(NIPAM) polymer grown on enzyme (various)		o/w and w/o	Benzoin condensation reaction between two benzaldehyde molecules, generation of H_2O_2 from glucose and subsequent production of methyl pentyl sulfoxide and production of cyclohexene	Various cascade reactions
109	Water	Toluene	*Alcaligenes faecalis* cells coated with porous calcium phosphate mineral shell and Fe_3O_4 nanoparticles. Sodium monododecyl phosphate then adsorbed on mineral shell (~ 5 μm)		o/w and w/o	Hydrolysis of hydrophobic (*R*,*S*)-mandelonitrile to hydrophilic *R*-(–)-mandelic acid	Magnetically-controlled reversible disassembly/assembly of particles at interfaces
110	Water	Various organic solvents	Dendrimer-like mesoporous SiO_2 modified with octyl, amino and thiol groups containing different catalytic groups (peptide, metal complex and DNAzymes) (90 nm)		o/w and w/o	Hydrolysis of *p*-nitrophenyl butyrate, H_2O_2 oxidation of (2-chloroethyl)ethyl sulfide	-
114	Water	Dichloromethane	TEMPO[x] immobilised in P((TMA-co-DMA)-b-MMA)[y] or in P(TMA-b-MMA)[z] (20-90 nm)		w/o and o/w	Alcohol oxidation	Destabilisation/re-emulsification by addition of CO_2 and N_2,

							respectively
101	Water	Various oils	Lipase from *Candida rugosa* adsorbed on chitosan nanogel (~ 50 nm)		o/w and w/o	Hydrolysis of *p*-nitrophenyl palmitate and triglycerides	-
84	Water	Dodecane	Ni/carbon nanotubes (7.4 nm)		o/w and w/o	Hydrogenation of furfural	-
36	Aqueous dextran (500 kDa)	Aqueous polyethylene glycol (PEG, 8 kDa)	Methoxy PEG-urease conjugate particles (200-500 nm)		Dextran-rich/PEG-rich	Hydrolysis of urea to ammonium carbonate	-
			Denatured methoxy PEG-urease conjugate particles (200-500 nm)	Urease			
37	Aqueous dextran (10 kDa)	Aqueous PEG (8 kDa)	Clay particles (kaolinite, montmorillonite and illite) (0.5-1.6 µm)		Dextran-rich/PEG-rich	Reaction of *o*-phenylenediamine with hydrogen peroxide to form 2,3-diaminophenazone	-
38	Aqueous dextran (10 kDa)	Aqueous PEG (8 kDa)	PEGylated liposomes (~130 nm)		Dextran-rich/PEG-rich	Ribozyme cleavage using a two-piece hammerhead ribozyme	-
48	1-Dodecene	[BMIM]BF_4[aa] or water	Non-porous and dendritic mesoporous SiO_2 modified with C18N[ab](~ 100 nm)	Rh-sulfo-xantphos	IL/o and w/o	Hydroformylation of 1-dodecene	Continuous flow reaction
43	Toluene	[BMIM]BF_4[aa]	$H_3PW_{12}O_{40}$ (HPA[m]) immobilised on poly(1-vinyl-3-ethylimidazolium		IL/o	Acylation of toluene with acetic	Continuous flow reaction

			bromide) functionalised silica@PS[ac]/PDVB[ad] Janus particles (500 nm)			anhydride	
45	[BMIM]BF_4[aa]	TMSCN[ae] in octane	Hydrophobic SiO_2 (40-60 nm)	[BMIM]Cl[af]	IL/o	Cyanosilylation of carbonyl compounds	Continuous flow reaction
46	[BMIM]PF_6[ag], [BMIM]BF_4[aa] and water	Octane	Hydrophobic SiO_2 (20 nm)	Various: CALB,[a] Cr^{III} (salen), [Pd(OAc)$_2$]	IL/o	Kinetic resolution of alcohols, asymmetric ring opening of epoxides and Tsuji-Trost reaction	Interfacial sol-gel process to grow a crust around IL droplets after emulsion preparation. Continuous flow reactions
47	Octane	[BIMIM]PF_6[aa]	DCDMS[o]-modified SiO_2 (40-60 nm)	CALB[a] (also CuI)	IL/o	Enantioselective trans-esterification of alcohols (also azide-alkyne cycloaddition)	Continuous flow reaction
51	Dodecyl aldehyde	Ethylene glycol	Activated charcoal functionalized with phenyl sulfonic groups (10 µm)		Dodecyl aldehyde/ethylene glycol	Acetalization of dodecyl aldehyde with ethylene glycol	Multistep reaction *via* hemiacetal intermediate
52	Glycerol (g)	Dodecanol (d)	PS[ac]-grafted SiO_2 bearing sulfonic acid centers (45-79 nm)		g/d, d/g and d/g/d	Etherification reaction of glycerol with dodecanol	Dodecanol conversion lower in d/g emulsions than in d/g/d and selected g/d emulsions
53	Vegetable oil	Methanol (MeOH)	SiO_2 functionalised with alkyl chains and active propylsulfonic acid residues (~7 nm)		MeOH/o	Transesterification of vegetable oils with MeOH	-
70	1-dodecyl aldehyde	Ethylene glycol	Amphiphilic SiO_2 bearing alkyl and propylsulfonic acid groups (150-300 nm)		Dodecyl aldehyde/ethylene	Acetalization of immiscible long chain fatty	-

				glycol	aldehydes with ethylene glycol	
23	Ethylene glycol	Dodecanal	SiO_2 nanoparticles modified with propylsulfonic acid groups and octyl chains (90-460 nm) with different surface roughness	Ethylene glycol/dodecanal	Acetalization reaction between dodecanal and ethylene glycol	-
115	Water	Ethyl acetate	Au nanoclusters/Sodium caseinate (micelles, 20-40 nm)	Ethyl acetate/w	Hydrogenation of p-nitroaniline	Emulsification/demulsification is pH dependent. Cyclability maintained over 100 cycles

[a] CALB: *Candida Antarctica* lipase B

[b] HIPE: High internal phase emulsion

[c] Rh-TPPTS: Rhodium-tris(m-sulfonatophenyl) phosphine

[d] Halloysite: Natural clay. Aluminosilicates with a molecular formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$. These have a tubular shape with silica tetrahedra outside and aluminium oxide octahedra inside

[e] HDPA: Hexadecylphosphate acid

[f] 8A PEG-CD: Cyclodextrin functionalized 8-arm poly(ethylene glycol)

[g] 8A PEG-Fc: Ferrocene functionalized 8-arm poly(ethylene glycol)

[h] ZIF-8: Zeolitic-imidazolate framework-8

[i] PEO: Poly(ethylene oxide)

[j] P4VP: Poly(4-vinylpyridine)

[k] TEOS: Tetraethyl orthosilicate

[l] CALA: *Candida Antarctica* lipase A

[m] HPA: Heteropolyacid

[n] TMODS: Trimethoxy(octadecyl)silane

[o] DCDMS: Dichlorodimethylsilane

[p] OTS: Octadecyltrichlorosilane

[q] EDA: Ethylenediamine

[r] TMOS: Tetramethoxysilane

[s] $[C_{12}]_3[PW_{12}O_{40}]$: Dodecyltrimethylammonium phosphotungstate

[t] P(NiPAM-*co*-MAA): Poly(*N*-isopropylacrylamide-*co*-methacrylic acid)

[u] P(NiPAM-*co*-NiPMAM): Poly(*N*-isopropylacrylamide-*co*-*N*-isopropylmethacrylamide) copolymer

[v] VPTT: Volume phase transition temperature

[w] PDEAEMA: Poly(2-(diethylamino)ethyl methacrylate)

[x] TEMPO: 2,2,6,6-Tetramethylpiperidine-1-oxyl

[y] P((TMA-co-DMA)-b-MMA): poly((2,2,6,6-tetramethylpiperidine-1-oxyl-4-methacrylate-co-(2-(dimethylamino) ethyl methacrylate))-b-methyl methacrylate)

[z] P(TMA-b-MMA): poly(2,2,6,6-tetramethylpiperidine-1-oxyl-4-methacrylate-b-methyl methacrylate)

[aa] $[BMIM]BF_4$: 1-Butyl-3-methylimidazolium tetrafluoroborate

[ab] C18N: Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride

[ac] PS: Polystyrene

[ad] PDVB: Polydivinylbenzene

[ae] TMSCN: Trimethylsilyl cyanide

[af] [BMIM]Cl: 1-Butyl-3-methylimidazolium chloride

[ag] $[BMIM]PF_6$: 1-Butyl-3-methylimidazolium hexafluorophosphate