Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information for the paper:

Catalytic Routes towards Acrylic Acid, Adipic Acid and ε-Caprolactam starting from Biorenewables

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ESI Table 1: Summary of various processes.

Substrate	Product	Catalyst	Conditions	X (%)	S (%)	Y (%)	Remarks	Ref. from review
Section 3. Acrylic acid								
propylene	acrylic acid	1) Bi/Mo–O 2) Bi/V–O	1) 320 °C 2) 280 °C	-	-	-	depends on large recycling, energy intensive	11, 47
ethanol	propylene	scandium-loaded In_2O_3	500 °C	-	-	60		49
glycerol	acrylic acid	1) ZSM–5, 300 °C 2) Mo–V–O/SiO_2	unknown	100	34	34		51
glycerol	acrylic acid	1) 90.7% ZrO_2 – 9.3% WO_3 2) $Mo_{12}V_{4.8}Sr_{0.5}W_{2.4}Cu_{2.2}O_x$	O_2, 280 °C	100	75	75	catalyst stability and reusability unknown	52, 53
starch	lactic acid	*Lactobacillus acidophilus* or *Streptococcus thermophiles*	fermentation	-	-	90		54, 55
lactic acid	acrylic acid	calcium pyrophosphate	375 °C, WHSV-3 h^{-1}	100	78	78		62, 63
lactic acid	2-acetoxy-propionic acid	H_2SO_4	AcOH	-	-	>90		65
glycerol	acrolein	mordenite	280 °C, 10 h	100	92	92	batch reaction	72
glycerol	acrolein	$CsSiW_{12}O_{40}/Al_2O_3$	250 °C, 3 h	100	96	96	continuous reaction	76
acrolein	acrylic acid	Mo–V–W–Cu–O/α-Al_2O_3	H_2O, O_2, N_2, 280 °C	98	92	90	fixed bed reactor	83
3-hydroxypropionic acid	acrylic acid	SiO_2	250 °C	100	97	97	20% aqueous feed	93
Section 4. Adipic acid								
cyclohexanol/ cyclohexanone	adipic acid	Cu^{II}, NH_4VO_3	50–60% HNO_3	-	-	-	process generates nitrous oxide waste	11, 105
cyclohexene	adipic acid	Na_2WO_4	microwave radiation, 90 min	-	-	68		110
phenol	cyclohexanone	Pd/(CaO/Al_2O_3)	140–170 °C, 1–2 bar H2	100	95	95		112
glucose	*cis,cis*-muconic acid	unknown	biosynthetic	-	-	24	recovery does not yield resin-grade product	113
cis,cis-muconic acid	adipic acid	Pt/C	H_2	-	-	97		113
glucose	levulinic acid	H_2SO_4 (5.0 wt%)	H_2O, 170 °C	-	-	81		119
levulinic acid	γ-valerolactone	ZrO_2	2-butanol, 150 °C, 16 h	-	-	92	alcohol both as solvent and hydrogen donor	123

γ-valerolactone	adipic acid	1) ZSM–5 2) bidentate diphosphine palladium	2) CO, H_2O	-	-	48		124
fructose	5-hydroxy-methylfurfural	Amberlyst–15	1,4-dioxane, 110 ˚C	98	92	90		127
5-hydroxy-methylfurfural	2,5-furandicarboxylic acid	hydrotalcite-supported gold nanoparticles	O_2	-	-	>99	substrate: catalyst ratio 40:1	133
2,5-furandicar-boxylic acid	tetrahydrofuran-2,5-dicarboxylic acid	Pd/SiO_2 (4% by weight)	52 bar H_2, 140 ˚C, 3 h	-	-	88		135
tetrahydrofuran-2,5-dicarboxylic acid	adipic acid	Pd/SiO_2 or Rh/SiO_2	HBr/HI, AcOH, 49 bar H_2, 160 ˚C, 3 h	-	-	99		135
glucose	glucaric acid	Pt/SiO_2	5 bar O_2 90 ˚C, 8 h	-	-	66		136
glucaric acid	adipic acid	Pd/Davisil 635	HBr, acetic acid 49 bar H_2 140 ˚C, 3 h	-	-	89	deactivation is a likely problem	136
succinic acid	1,4-butanediol	1% Pd–4% Re/TiO_2	69 bar H_2, 200 ˚C	99	90	89		145
1,4-butanediol	adipic acid	$Rh(PPh)_3COCl$ CH_3I promoter	AcOH 48 bar CO, 175 ˚C	100	74	74		146
Section 5. ε-Caprolactam								
cyclohexanone	ε-caprolactam	-	1) $NH_2O.H_2SO_4$ 2) H_2SO_4 2) NH_3	-	-		two steps, generating ammonium sulfate waste	11
lysine	ε-caprolactam	-	1)1,2-propanediol 187 ˚C, 2 h 2) KOH, NH_2OSO_3H –5 ˚C	-	-	75		155, 156
ethanol	1,3-butadiene	MgO/SiO_2 (1:1), Na_2O (0.1%)	350 ˚C	100	87	87		159
adiponitrile	6-aminocapronitrile	[Co–Mn–P–Na–O]	NH_3, 200 bar H_2	-	50	50	depends on feedstock recycling	169
6-aminocapronitrile	ε-caprolactam	-	H_2O, EtOH 70 bar, 220 ˚C, 15 min	-	-	79		169
6-aminocaproic acid	ε-caprolactam	-	12 bar 300 ˚C, 5 h	-	-	99	continuous = 95%	179, 180
adipamide	ε-caprolactam	8.6% Pd/Davisil 635 (5mol%)	diglyme, 250 ˚C, 2 h 1) 3.4 bar NH_3 2) 110 bar H_2	83	42	35		157
cis,*cis*-muconic acid	ε-caprolactam	5% Pd/Al_2O_3 (5 mol%)	dioxane, 250 ˚C, 2 h 1) 3.4 bar NH_3, 2) 34 bar H_2	79	70	55		158