Supporting Information for the article:

Designing effective solid catalysts for biomass conversion: Aerobic oxidation of ethyl lactate to ethyl pyruvate

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http://hims.uva.nl/hcsc

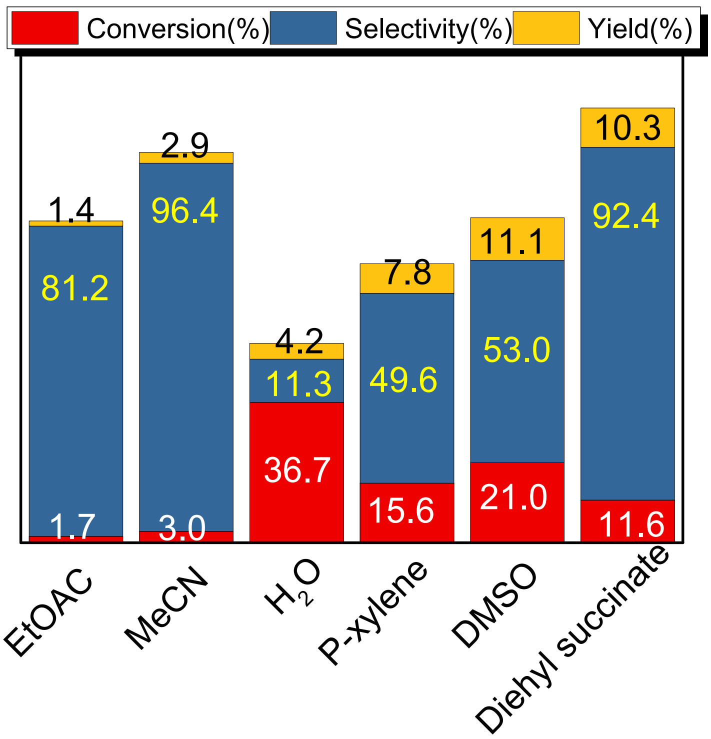

Figure S1 Effect of reaction solvent for the oxidative dehydrogenantion of ethyl lactate to ethyl pyruvate, reaction conditions: ethyl lactate 5 mmol, VO_x/C 25 mg (0.15 mol% V), 1 atm O_2, solvent, 1 ml, 100 °C, 4h.

Table S1. Influence of Brønsted / Lewis base on oxidation of ethyl lactate to ethyl pyruvate reaction.[a]

Entry	Additive	pK_b	Conversion (%)[b]	Product selectivity (%) [b]					Ethyl pyruvate yield (%)
				Ethyl pyruvate	acetaldehyde	ethanol	AcOH	others	
1	—	—	11	86	1	3	1	10	9
2	NaOH	0.2	7	30	5	51	2	13	2
3	Na_2CO_3	3.7	7	2	3	57	0	38	0
4	$NaHCO_3$	7.9	6	46	6	32	1	15	3
5	$NaHSO_4$	12	12	94	1	3	0	2	11
6	Piperidine	2.7	18	89	1	7	0	3	16
7	Diethylamine	2.9	19	84	1	13	0	2	16
8	Pyridine	8.8	31	93	1	3	1	2	29
9	Aniline	9.4	11	89	1	5	0	6	10

[a] Reaction conditions: ethyl lactate 5 mmol, additive 5 mol%, VO_x/C 25 mg (0.15 mol% V), 1 atm O_2, diethyl succinate (solvent, 1 ml), 130 °C, 1 h. [b] Determined by GC using biphenyl as an internal standard.

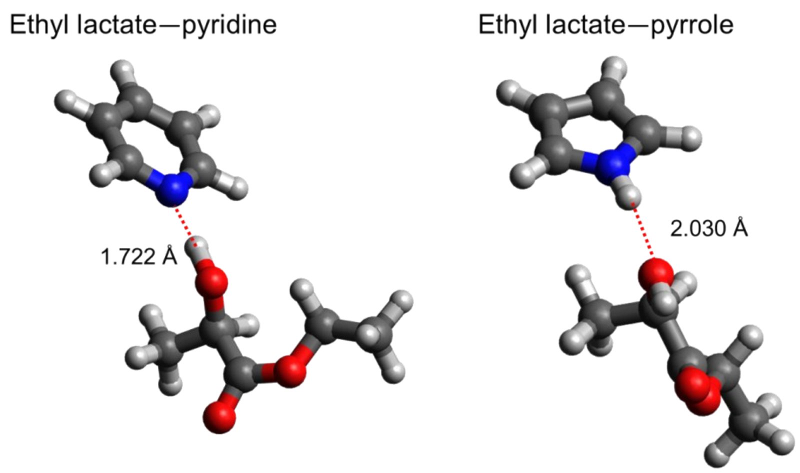

Figure S2. The Optimized geometries: ethyl lactate interacts with pyridine; ethyl lactate interacts with pyrrole.

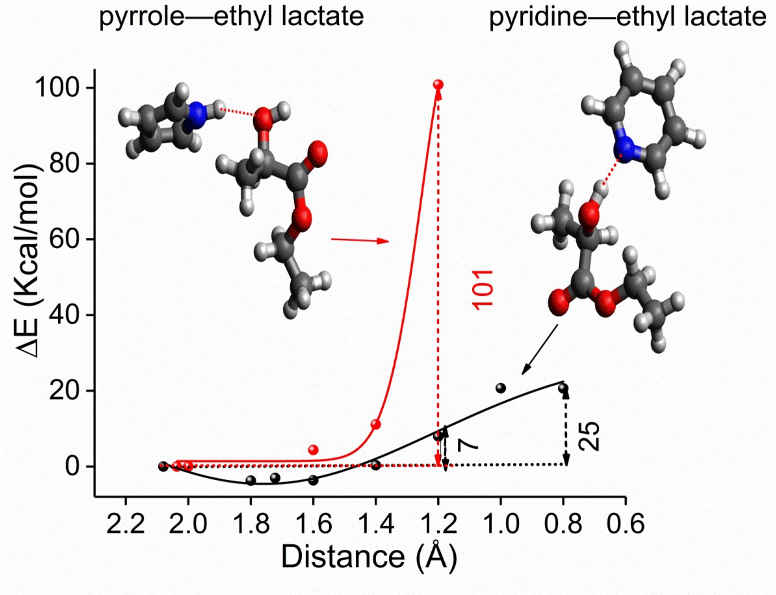

Figure S3. The relative potential energy plotted against the distance between ethyl lactate and pyridine and pyrrole, respectively. At each step, we first fixed the distance, and then calculated the potential energy of the optimized geometry (see Figure 3). At long distances, the interaction energy approaches zero. Here we assign the zero point distance as 2.3 Å. Shortening the distance from 2.3 Å to 1.2 Å gives energy barriers of 7 kcal/mol and 101 kcal/mol for EL–pyridine and EL–pyrrole, respectively. Indeed, even at a distance of only 0.8 Å the energy barrier for EL–pyridine increases only to 25 kcal/mol.) This higher energy barrier in the case of pyrrole can explain why pyrrole compounds supress the reaction, while, pyridine helps to catalyse it.

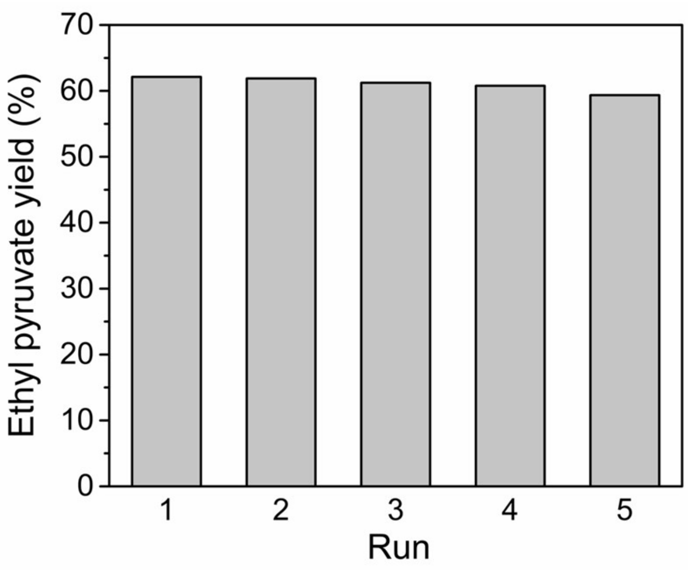

Figure S4. Recycling of VO_x/P4VP catalyst in the oxidation of ethyl lactate to ethyl pyruvate. Reaction conditions: ethyl lactate 5 mmol, catalyst: VO_x/P4VP 25 mg, 1 atm O_2, diethyl succinate (solvent, 1 ml). 130 °C, 4 h.

Table S2. Catalytic activity of analogous heterogeneous catalyst systems for the liquid-phase oxidation of lactate to pyruvate.

Entry	Catalyst	Oxidant	lactate type	additive	Temp. (°C)	Pressure (MPa)	Time	Sel. (%)	Yield (%)	Journal Year	Ref.
1	TiO_2	O_2	ethyl lactate	-	130	1	6h	75	37.5	Green Chem., 2014	1
2	3Pb-1Pt/C	H_2O_2	lactic acid	LiOH	90	0.1	20 min	91.3	60	Appl.Catal.A, 2017	2
3	Hemoglobin -NaD^+	H_2O_2	sodium lactate	phosphate buffer	30	0.1	50h	94	81	ChemSusChem, 2017	3
5	TS-1	H_2O_2	ethyl lactate	-	50	0.1	9h	97.8	97.8	ACS Catal. 2018	4
4	VTN	O_2	ethyl lactate	-	130	0.1	3h	91	47.3	ACS Catal. 2018	5
6	VO_x/P4VP	O_2	ethyl lactate	-	130	0.1	8h	90	75.6	This work	-

References

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