Supplementary Material for the paper

Heterogeneous chemistry of monocarboxylic acids on α–Al_2O_3 at ambient condition

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Table S1. Assignment of the vibrational frequencies (cm^{-1}) for adsorbed carboxylates following exposure of Al_2O_3 particles surfaces to carboxylic acids.

Surface species	Absorbance bands	Vibrational mode assignment
Adsorbed formate species[a]		
	1378	C–H in plane bend
	1393	OCO symmetric stretch
	1600	OCO antisymmetric stretch
	2750	OCO symmetric stretch and C–H in plane bend
	2866	C–H stretch
	2985	OCO symmetric stretch and C–H in plane bend
Adsorbed acetate species[b]		
	1343	symmetric bend of CH_3
	1424	deformation mode of CH_3
	1468	OCO symmetric stretch
	1578	OCO antisymmetric stretch
	2935	CH_3 symmetric stretch
	2986	C–H antisymmetric stretch
	3016	C–H antisymmetric stretch
Adsorbed propionate species[c]		
	1259	out–of–phase twisting of CH_2
	1303	in–plane wagging mode of CH_2
	1383	symmetric deformation of CH_3
	1424	asymmetric bending of CH_3 and OCO symmetric stretch
	1478	antisymmetric deformation of CH_3, scissoring modes of CH_2, and OCO symmetric stretch
	1568	OCO antisymmetric stretch
	2886	C–H symmetric stretch of CH_2
	2946	C–H symmetric stretch of CH_3
	2981	C–H antisymmetric stretch of CH_2

[a] from Chauvin et al. (1990), Amenomiya (1979), and Walmsley et al. (1981).

[b] from Chen and Bruce (1995) and Walmsley et al. (1981).

[c] from Yang et al. (2006), Kakihana and Akiyama (1987), and Yuzawa et al. (1997).

Table S2. Structural parameters and vibration frequencies (in cm^{-1}) for the calculated model formates I-III, calculated at B3LYP/6-311++G(3df,3pd) level of theory.

Mode	Optimized structural parameters					Vibrational mode		
	Bond length (Å)			Angle (degrees)		Calculated frequencies (cm^{-1})		
	C-O1	C-O2	Al1-O2	O1-C-O2	Al1-O2-C	δ(CH)	ν_s (OCO)	ν_{as} (OCO)
Monodentate	1.22	1.31	1.78	125.8	126.0	1405 (1367)	1304 (1268)	1698 (1651)
Bidentate	1.27	1.27	1.89	116.8	86.1	1296 (1260)	1400 (1362)	1556 (1513)
Bridging	1.25	1.26	1.86	126.6	134.0	1422 (1383)	1432 (1393)	1651 (1606)

Table S3. Structural parameters and vibration frequencies (in cm^{-1}) for the calculated model acetates I-III, calculated at B3LYP/6-311++G(3df,3pd) level of theory.

Mode	Optimized structural parameters					Vibrational mode		
	Bond length (Å)			Angle (degrees)		Calculated frequencies (cm^{-1})		
	C-O1	C-O2	Al1-O2	O1-C-O2	Al1-O2-C	δ(CH)	ν_s (OCO)	ν_{as} (OCO)
Monodentate	1.23	1.32	1.78	123.4	126.6	1410 (1371)	1344 (1307)	1690 (1644)
Bidentate	1.28	1.28	1.91	114.9	87.1	1444 (1404)	1468 (1428)	1529 (1487)
Bridging	1.26	1.26	1.84	124.0	131.2	1470 (1430)	1513 (1472)	1616 (1572)

Table S4. Structural parameters and vibration frequencies (in cm^{-1}) for the calculated model propionates I-III, calculated at B3LYP/6-311++G(3df,3pd) level of theory.

Mode	Optimized structural parameters					Vibrational mode		
	Bond length (Å)			Angle (degrees)		Calculated frequencies (cm^{-1})		
	C-O1	C-O2	Al1-O2	O1-C-O2	Al1-O2-C	$\delta(CH_3)+\nu_s(OCO)$	$\delta(CH_3)+\nu_s(OCO)$	$\nu_{as}(OCO)$
Monodentate	1.23	1.32	1.77	123.3	126.5	1284 (1249)	1408 (1369)	1686 (1640)
Bidentate	1.28	1.28	1.87	114.7	87.1	1449 (1409)	1525 (1483)	1508 (1467)
Bridging	1.27	1.26	1.84	123.8	135.7	1493 (1452)	1514 (1473)	1608 (1564)