

Table S1. Assignment of IR bands in Figure 3

<i>Frequency, cm⁻¹</i>	<i>Material</i>	<i>Assignment</i>	<i>Ref.</i>
Bands resulting from C₂H₅COOH adsorption (spectra reported as blue lines)			
1550-1495	TiO ₂ _P25		
1600, 1540	ZrO ₂		
1556	TiO ₂ _Merck	$\nu_{\text{asym}}\text{COO}^-$	26,27
1600-1500,	CeO ₂		
1635, 1576	Al ₂ O ₃		
1450-1400	TiO ₂ _P25		
1440, 1418	ZrO ₂		
1450-1400	TiO ₂ _Merck	$\nu_{\text{sym}}\text{COO}^-$	26, 27
1425	CeO ₂		
1450, 1418	Al ₂ O ₃		
1473	TiO ₂ _P25, ZrO ₂ , TiO ₂ _Merck		
1468	CeO ₂ ,	$\delta_{\text{asym}}\text{CH}_3 + \delta_{\text{sym}}\text{CH}_2$	28
1480	Al ₂ O ₃		
1380	all oxides	$\delta_{\text{sym}}\text{CH}_3$	28
1670	TiO ₂ _Merck, Al ₂ O ₃	$\nu\text{C=O}$, undissociated C ₂ H ₅ COOH	26, 27
Bands resulting from subsequent adsorption of C₂H₅COOH + CH₃(CH₂)₄NH₂ (spectra reported as grey lines)			
1590	TiO ₂ _P25	$\nu\text{C=O}$ (amide)	28
1530	TiO ₂ _P25		
1600, 1540	ZrO ₂		
1616, 1556	TiO ₂ _Merck	$\nu_{\text{asym}}\text{COO}^-$	26, 27
1600-1500,	CeO ₂		
1644, 1635, 1576	Al ₂ O ₃		
1415	TiO ₂ _P25		
1440, 1418	ZrO ₂		
1450-1400	TiO ₂ _Merck	$\nu_{\text{sym}}\text{COO}^-$	26, 27
1425	CeO ₂		
1450, 1418	Al ₂ O ₃		
1560	TiO ₂ _Merck		
1582	Al ₂ O ₃	δNH_2	28
1469	TiO ₂ _P25,		
1474	ZrO ₂ ,		
1470	TiO ₂ _Merck	$\delta_{\text{asym}}\text{CH}_3 + \delta_{\text{sym}}\text{CH}_2$	28
1368	CeO ₂ ,		
1471	Al ₂ O ₃		
1380	all oxides	$\delta_{\text{sym}}\text{CH}_3$	28

Table S2. Assignment of IR bands in Figure 4

<i>Frequency, cm⁻¹</i>	<i>Material</i>	<i>Assignment</i>	<i>Ref.</i>
Bands resulting from HCOOH adsorption (spectra reported as blue lines)			
1580-1541	TiO ₂ _P25		
1566	ZrO ₂		
1598	TiO ₂ _Merck	$\nu_{\text{asym}}\text{COO}^-$	18, 26, 27
1586, 1550,	CeO ₂		
1628, 1600	Al ₂ O ₃		
1412, 1361	TiO ₂ _P25		
1370-1316	ZrO ₂		
1403, 1364	TiO ₂ _Merck	$\nu_{\text{sym}}\text{COO}^-$	18, 26, 27
1371, 1361, 1307	CeO ₂		
1391, 1324	Al ₂ O ₃		
1385	TiO ₂ _P25, ZrO ₂		
1386	TiO ₂ _Merck	$\delta\text{O-C-H}$	18, 26, 27
1380	CeO ₂ , Al ₂ O ₃		
1673	TiO ₂ _Merck	$\nu\text{C=O}$,	
1675	Al ₂ O ₃	undissociated HCOOH	18, 26, 27
Bands resulting from subsequent adsorption of CH₃(CH₂)₄NH₂ (spectra reported as grey lines)			
1665, 1634	TiO ₂ _P25		
1674, 1636	ZrO ₂		
1665, 1643	TiO ₂ _Merck	$\nu\text{C=O}$ (amide)	18, 28
1666, 1629	CeO ₂		
1653	Al ₂ O ₃		
1589	TiO ₂ _P25		
1573	ZrO ₂ , CeO ₂		
1598	TiO ₂ _Merck	$\nu_{\text{asym}}\text{COO}^-$, δNH_2	18, 26, 28
1603, 1528	Al ₂ O ₃		
1469, 1444	TiO ₂ _P25		
1466, 1447	ZrO ₂ ,		
1466, 1441	TiO ₂ _Merck	δCH_2 , δCH_3	28
1464	CeO ₂		
1469	Al ₂ O ₃		
1361,	TiO ₂ _P25		
1370-1316	ZrO ₂		
1386, 1364	TiO ₂ _Merck	$\nu_{\text{sym}}\text{COO}^-$	18, 26
1375	CeO ₂		
1383, 1300	Al ₂ O ₃		

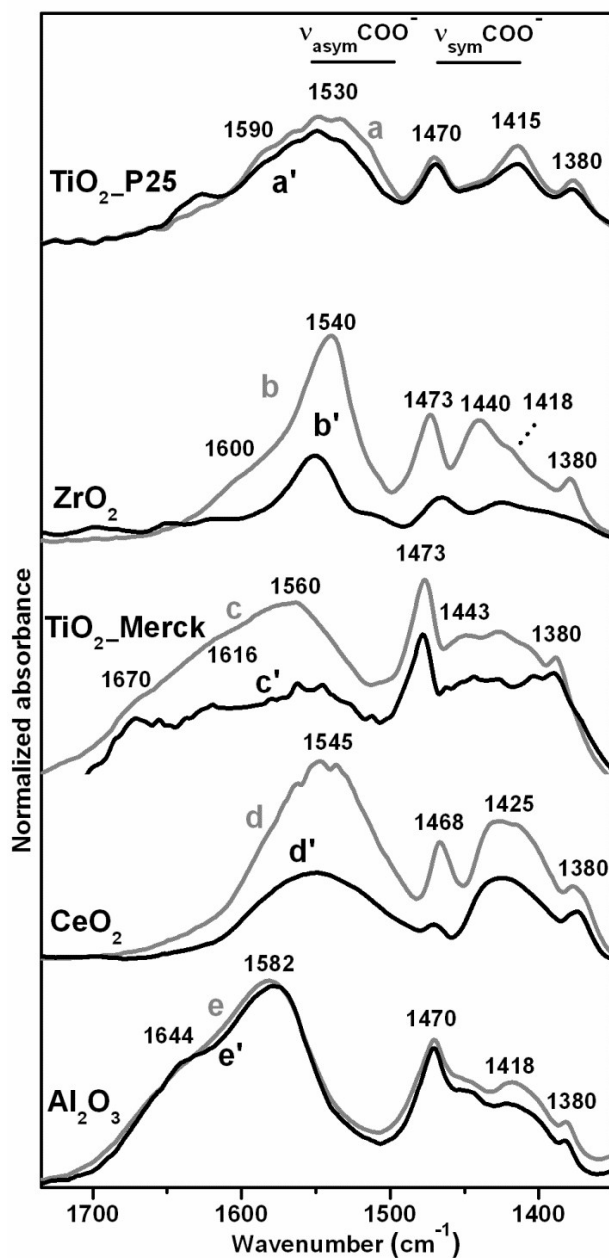


Figure S1. IR spectra of TiO_2 _P25, ZrO_2 , TiO_2 _Merck, CeO_2 , and $\gamma\text{-Al}_2\text{O}_3$ contacted with propanoic acid and 1-pentanamine, outgassed at r.t. (grey lines: a, b, c, d, e) and further heated in static atmosphere at 383K for 30 min (black lines: a', b', c', d', e').

Table S3. Integrated intensities of $\nu_{\text{asym}}\text{COO}^-$ and $\nu_{\text{sym}}\text{COO}^-$ components of HCOOH adsorbed on $\text{TiO}_2\text{-P25}$ and $\text{TiO}_2\text{-Merck}$ (see Figure 5 in the main text).

<i>Material</i>	$\nu_{\text{asym}}(\text{COO}^-)$, <i>cm⁻¹</i>	<i>Integrated Intensity, cm⁻¹</i>	$\nu_{\text{sym}}(\text{COO}^-)$, <i>cm⁻¹</i>	<i>Integrated Intensity, cm⁻¹</i>
TiO₂_P25	1519	5.43	1361	10.19
	1541	8.60	1412	0.28
	1560	4.35		
	1579	11.53		
	1615	5.98		
TiO₂_Merck	1598	29.74	1364	3.90
	1674	12.50	1403	2.07

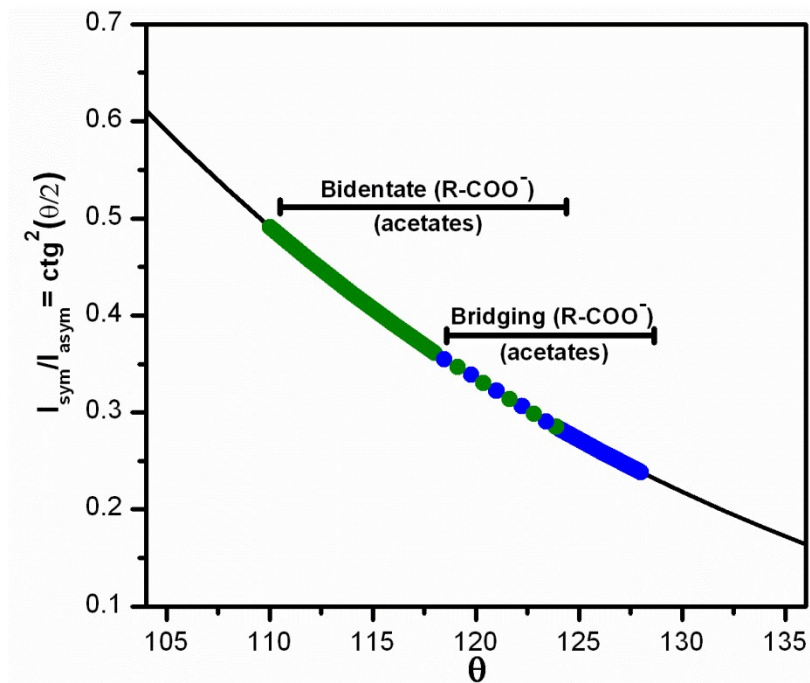


Figure S2. Dependence of integrated intensities ratio of $I(\text{COO}_{\text{sym}})/I(\text{COO}_{\text{asym}})$ from the O-C-O bond angle of adsorbed COO^- species (in green and blue are ranges of angles measured for bidentate and bridging type of carboxylate complexes respectively). [Ref: G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.*, 1980, 33, 227]