

Supporting Information for

# The Hydrogenation of Carbon Dioxide by Water: Alkali-Promoted Synthesis of Formate

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## EXPERIMENTAL METHOD

Experiments were performed in a three level UHV chamber (base pressure  $2 \times 10^{-10}$  Torr), which contained facilities for IRAS, Low Energy Electron Diffraction, Auger Electron Spectroscopy and TPD. Vibrational spectra were obtained with a Bruker IFS/66v FTIR spectrometer at a resolution of  $4 \text{ cm}^{-1}$  by typically co-adding 100 scans. Potassium was evaporated from a SAES Getter source onto a Cu(111) single crystal surface. A sample mount allowed cooling to 100 K and heating to 1200 K using a programmable temperature controller.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were introduced by backfilling the UHV chamber to partial pressures of typically  $2 \times 10^{-8}$  Torr each. Details of verifying the

cleanliness of the potassium film and calibration of the film thickness are described in details elsewhere.<sup>17</sup>

Thermal desorption data were collected in a line-of-sight geometry using a heating rate of 2 K/s; we also monitored desorbing species simultaneously with the IRAS data collection during annealing experiments where the sample is not facing the mass spectrometer. In this mode of TPD operation the positions of desorption peaks shifted to lower temperature due to lower heating rate (0.5 K/s vs 2 K/s).

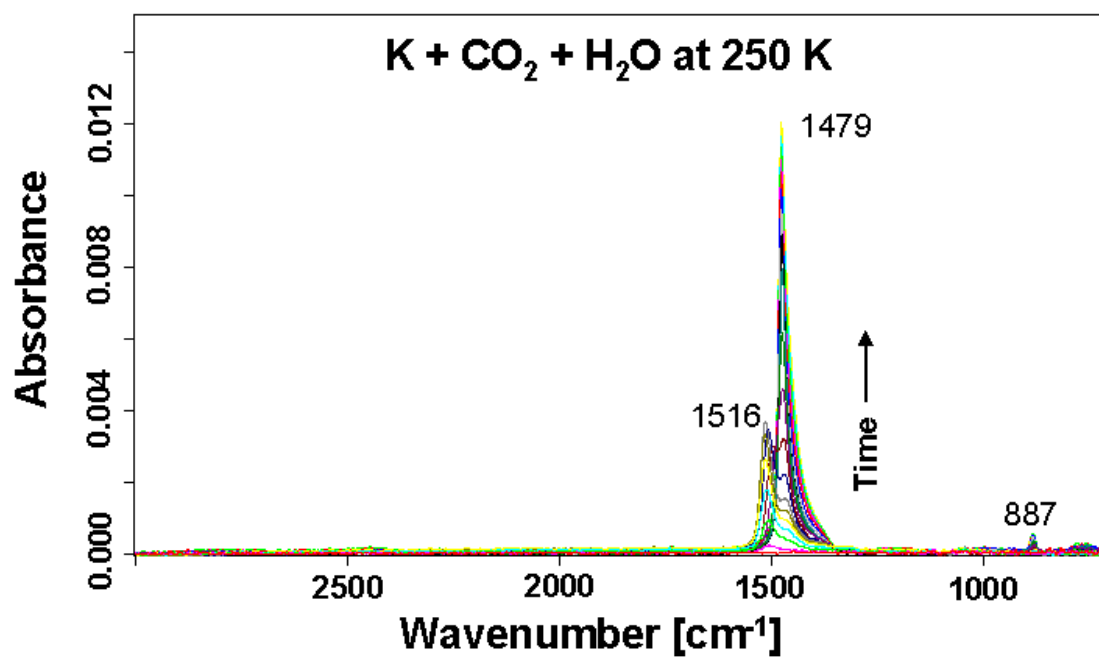


Figure S1: Time-evolved FTIR spectra obtained during the reactive evaporation of potassium in the presence of H<sub>2</sub>O and CO<sub>2</sub> on Cu(111) at 250 K. Spectra have been collected at 50s time intervals, but only every second spectrum is shown. (K-deposition rate: 0.002 ML/s)

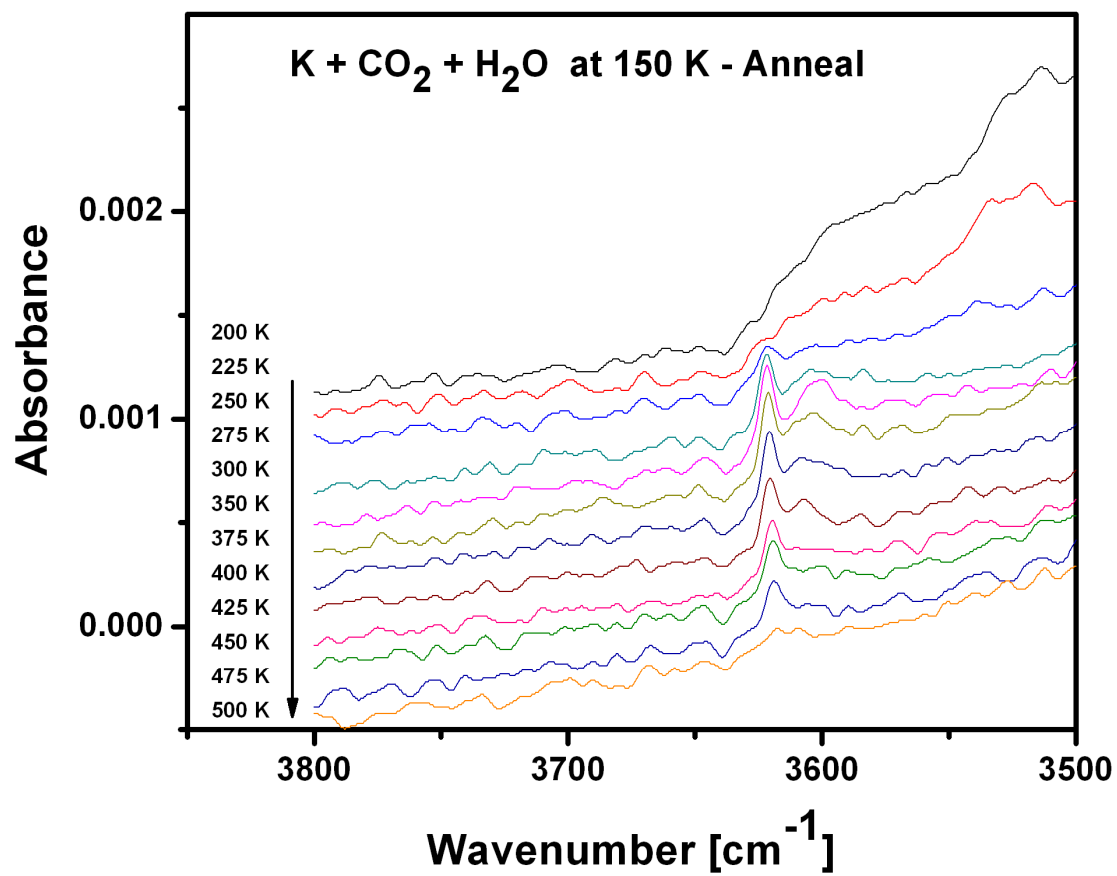


Figure S2: Time-evolved FTIR spectra of formate obtained during annealing from 200 to 500 K with heating rate of 0.5 K/s.

	$C_{2v}$	Crystalline Bulk HCOOK [cm <sup>-1</sup> ] Ref. (1)	HCOOH / multilayer K/Ru(001) [cm <sup>-1</sup> ] Ref. (2)	HCOOH / multilayer K/Co{101_0} [cm <sup>-1</sup> ] Ref. (3)	HCOOK this work [cm <sup>-1</sup> ]	
					150 K	250 K
$\nu(\text{CH})$	$A_1$	2808	2780	2780	2785	2770
$2\delta(\text{CH})$		2730	2693	2692	2696	2688
$\nu_a(\text{OCO})$	$B_1$	1597	1643	1614 - 1637	1619	1634
$\delta(\text{CH})$	$B_1$	1389	1385		1388	
$\nu_s(\text{OCO})$	$A_1$	1357	1364	1366	1367	1361
$\pi(\text{CH})$	$B_2$	1062	-	-	-	-
$\delta(\text{OCO})$	$A_1$	772	764	764	766	761

Table T1: Vibrational mode assignments of potassium formate

	HCOOK [cm <sup>-1</sup> ] this work	Oxalate C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> [cm <sup>-1</sup> ] Ref. (4)      this work		Carbonate CO <sub>3</sub> <sup>2-</sup> [cm <sup>-1</sup> ] Ref. (5)      this work	
v(CH)	2785				
v <sub>a</sub> (OCO)	1619	1642	1665	1447	1460
v <sub>s</sub> (OCO)	1367	1320	1315	1071 (v.w.)	-
π(CO)*				884 (v.w.)	882
δ(OCO)	766	768	767	764	-

\* out-of-plane OCO<sub>2</sub> motion = rock      v.w. = very weak

Table T2: Vibrational mode assignments of potassium compounds observed during heating of the multilayer

#### References

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