Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Liquid Phase CO_2 Hydrogenation to Formate Using Palladium and Ruthenium Nanoparticles Supported on Mo_2C

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Table S1: Reported heterogeneous catalysts for the CO_2 hydrogenation to formate salts under aqueous alkaline conditions

Catalyst	**Base**	**pCO_2+pH_2 (MPa)**	**Temperature (^oC)**	**TOF (h^{-1})**	**Literature Source**
Pd/Chitin	NaOH	4	60	257	[1]
Pd/g-C_3N_4	none	5	40	95	[2]
PdAg/TiO_2	$NaHCO_3$	2	100	31	[3]
Pd/TiO_2	$NaHCO_3$	2	100	12	3
Pd_3Ni_7/CNT-GR	none	5	40	$7.2x10^{-3}$	[4]
Ru/LDH	NaOH	2	100	29	[5]
Rh-HT	none	5	60	660	[6]

PXRD pattern in Figure S1 confirms the formation of beta molybdenum carbide. Eight major reflections at 2θ ≈ 34, 38, 39, 52, 62, 69.5, 74, and 75 corresponding to the crystal planes (100), (002), (101), (102), (110), (103), and (112) respectively of β-Mo_2C are observed respectively, indicating a high degree of crystallinity. The formation of this hcp phase is consistent with the reference to the JCPS 001-1188 PDF file and previous publication. Because of low metal loading, Pd or Ru peaks are not detected.

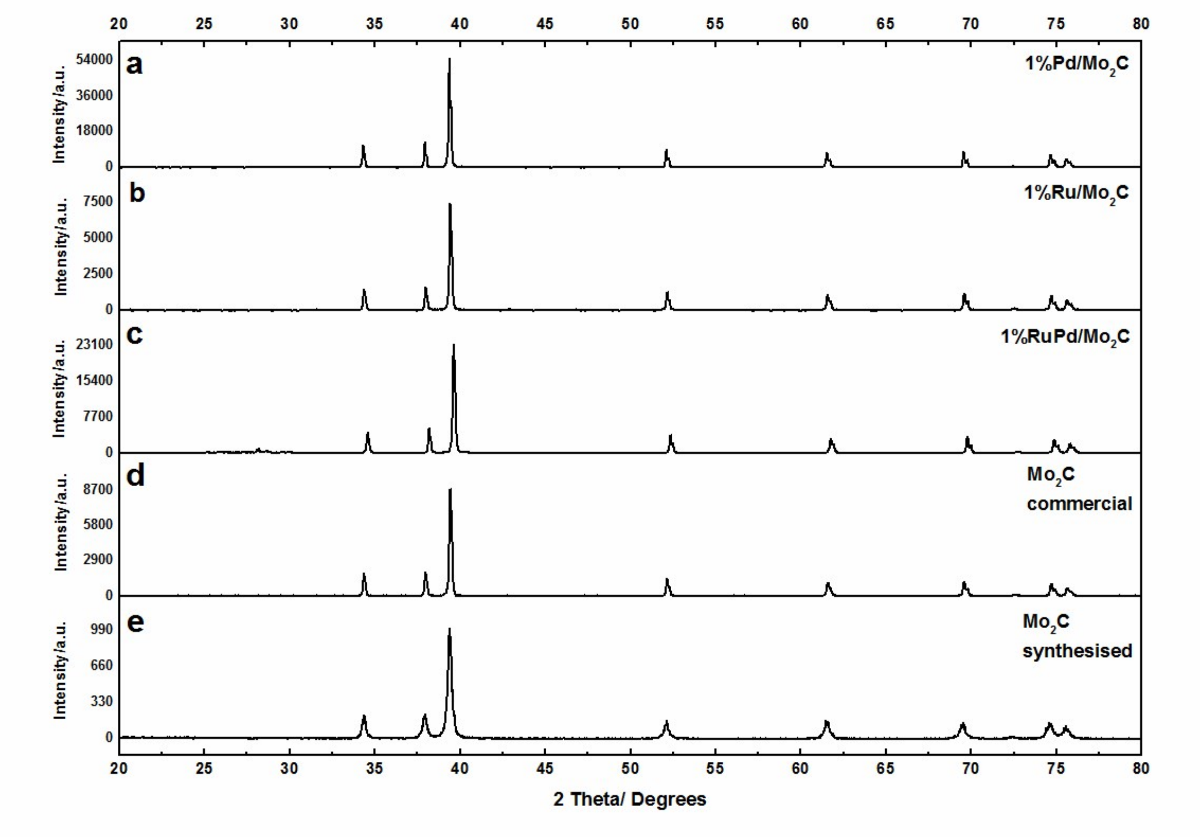


Figure S1: Powder XRD patterns for [a] 1% Pd/Mo_2C-MIm (0.58) [b] 1% Ru/Mo_2C and [c] 1% RuPd/Mo_2C [d Mo_2C (commercial) [e] Mo_2C (lab synthesised)

Table S2: Formate productivity using different Pd/Mo_2C catalysts [a]

Catalyst	**Pd loading (wt. %)**	**Formate (mmol)**
1% Pd/Mo_2C-MIm (0.58M)	1.09 [b]	1.09
5% Pd/Mo_2C-MIm	5.16 [b]	2.14
1% Pd/Mo_2C- MIm (2M)	1.02 [b]	1.53
1% Pd/Mo_2C-SIm	0.80 [b]	0.39
1% Pd/CeO_2	1.00	0.204

[a] Reaction conditions: Pd/Mo_2C, Pd/CeO_2: 150 mg; 1M aqueous NaOH: 15 ml; pCO_2: 10 bar (at 25 °C); pH_2: 10 bar (at 25 °C); reaction temperature: 100 °C; reaction time: 19 h. [b] Determined by MP-AES. Catalysts were digested in aqua regia to dissolve the metal and diluted in H_2O prior to analysis

Table S3: Pd weight percentages of catalysts during stability study, calculated using MP-AES

	Weight Percentage			
Re-use	**1% Pd/Mo_2C -MIm (2M)**	**1% Pd/Mo_2C -MIm (0.58M)**	**1% $RuPd/Mo_2C$**	**1% Pd/Mo_2C -Sy**
Fresh	1.02	1.09	0.99	1.02
1st	1.05	1.13	0.96	1.01
2nd	1.07	1.15	1.00	1.12

Catalysts were digested in aqua regia to dissolve the metal and diluted in H_2O prior to analysis

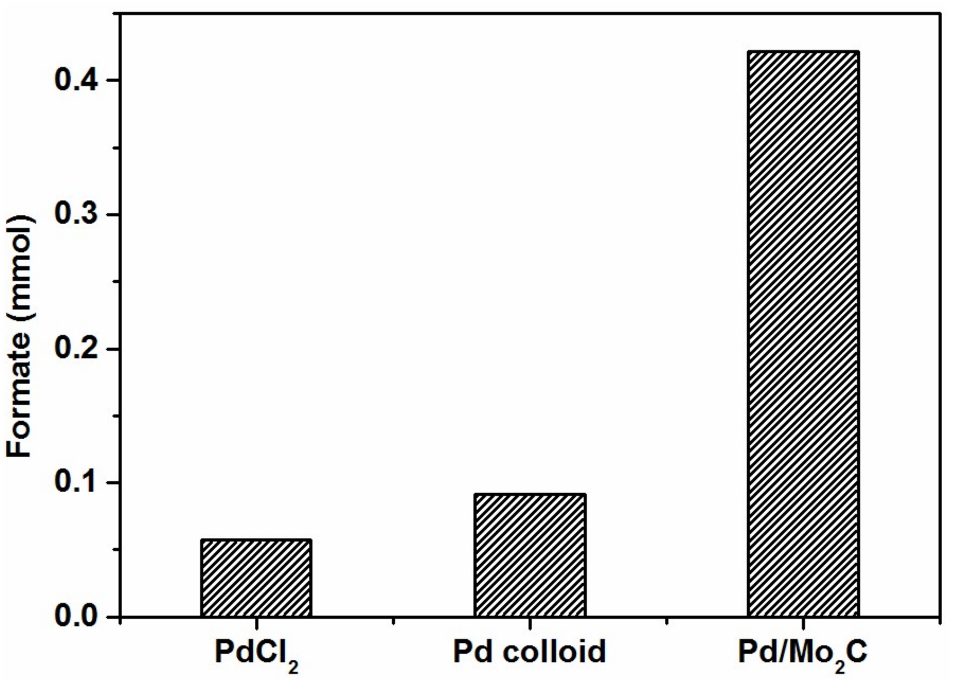
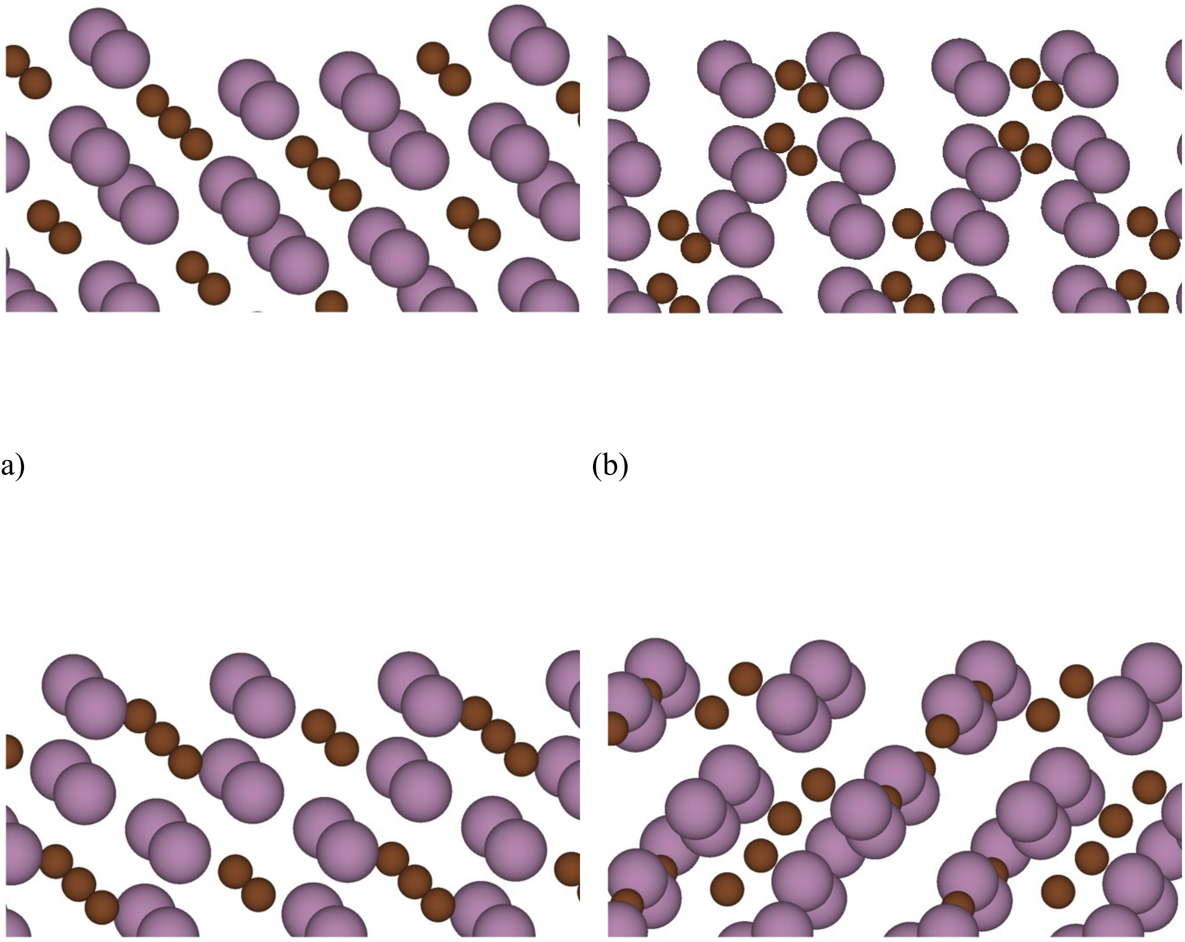


Figure S2: Elemental Pd in solution testing to confirm that metal-support interactions are improving the activity for CO_2 *hydrogenation. Reaction conditions in 10ml stainless steel autoclave: Pd: 0.4mg; 1M NaOH: 4ml;* pCO_2*: 10 bar (at 25 °C);* pH_2*: 10 bar (at 25 °C); reaction temperature: 100°C; reaction time: 19h.*



(a) (b)

(c) (d)

Figure S3: (a) (001), (b) (010), (c) (011) and (d) (101) surfaces of Mo_2C*. Colour code: Mo–large purple spheres, C–small brown spheres.*

Table S4: Energies of the different surfaces of Mo_2C*.*

Surface	**γ (meV/Å^2)**
(001)	227
(010)	186
(011)	206
(101)	171

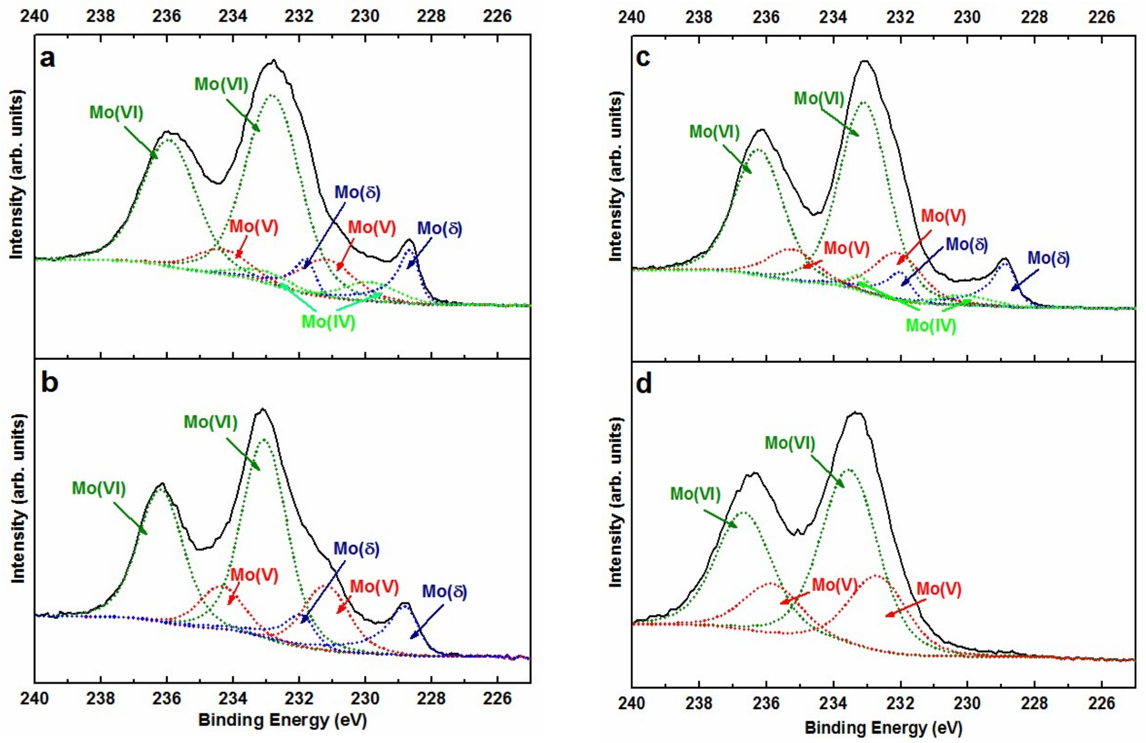


Figure S4: Mo 3d XPS spectra of 1% Pd/Mo_2C-MIm (2M) [a] fresh sample [b] used sample and 1% RuPd/Mo_2C [c] fresh sample [d] used sample

X-ray photoelectron spectroscopic data (Mo 3d) of 1% Pd/Mo_2C-MIm (2M) (Figure S2 a & b) reveals that the support is predominantly oxidised with several oxidation states of molybdenum ranging from Mo($^{\delta+}$) to Mo($^{6+}$) ($1<\delta<4$). The two main peaks at 232.8 and 235.9 eV can be attributed to the $3d_{5/2}$ and $3d_{3/2}$ transitions of Mo^{6+}, in MoO_3. Molybdenum carbide found at peaks 232.87 and 232.1 eV, attributed to the transitions of $3d_{5/2}$ and $3d_{3/2}$ transitions of $Mo^{\delta+}$ [7]. A number smaller peaks are found in the range 235-240 eV which are attributed to molybdenum oxides of lower Mo valency, or more likely Mo^{5+}/Mo^{4+} oxycarbides. Similar results are obtained by Griboval-Constant *et al* [8] and Xiang *et al* [9]. The presence of these partial and/or total oxidation species of molybdenum can be attributed to surface oxidation and/or passivation of the catalyst prior to exposure to air during the Mo_2C synthesis [9]. It should be mentioned that no bulk MoO_2 or MoO_3 is found by XRD [10]. 1% RuPd/Mo_2C presents a similar Mo 3d XPS spectra (Figure S2c) to 1% Pd/Mo_2C-MIm (2M), revealing a range of molybdenum carbide and molybdenum oxide species. However, a used 1% RuPd/Mo_2C sample (Figure S2d) has no carbide visible, suggesting a thick oxide film at the surface greater than 10nm.

To calculate the activation energy (E_a), rates of conversion of substrate at different temperatures are required. In our system, quantification of CO_2 and H_2 is extremely challenging. Hence, we have used formate concentration to calculate the rate of the reaction since formate is the only product detected and we are assuming 100% selectivity. The rate constants were calculated for three different temperatures: 75, 100 and 125 °C for both monometallic Pd/Mo_2C and bimetallic RuPd/Mo_2C catalysts.

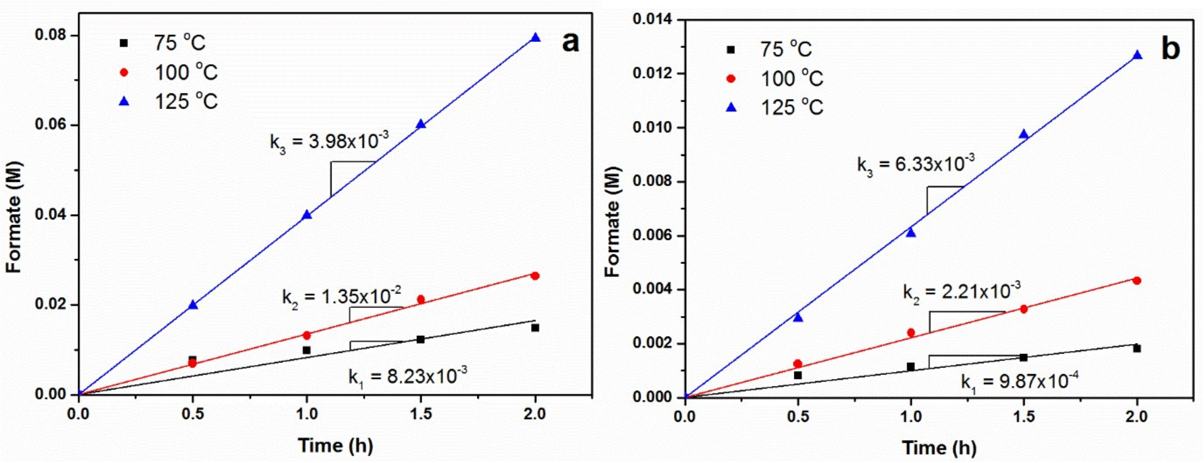


Figure S5. Effect of temperature on the catalytic hydrogenation of CO_2 using (a) 1% Pd/Mo_2C-MIm (2M) (b) 1%RuPd/Mo_2C at 75, 100 and 125°C and varying reaction times. Reaction conditions: catalyst 150 mg (monometallic, 0.014mmol (Pd); bimetallic, 0.007mmol (Pd, Ru)); 1M aqueous base: 15 ml; pCO_2: 10 bar (25 °C); pH_2: 10 bar (25 °C)

The activation energy E_a of the reaction can be determined using the Arrhenius equation, by plotting lnk and $1/T$, as shown in Figure S6.

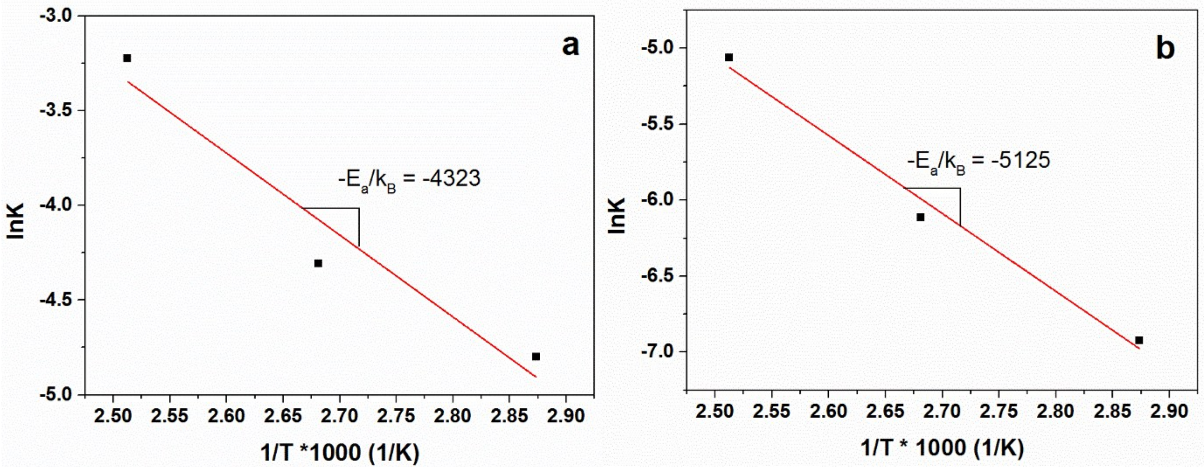


Figure S6. Arrhenius plot of the temperature dependence of the rate constant for (a) 1%Pd/Mo2C-MIm (2M) (b) 1%RuPd/Mo$_2$C.

Activation energies for the catalysts 1%Pd/Mo$_2$C-MIm (2M) and 1%RuPd/Mo$_2$C are :

Pd/Mo$_2$C	+35.9 kJ/mol
RuPd/Mo$_2$C	+42.6 kJ/mol

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