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Electronic Supplementary Information

Photochemical Reduction of Carbon Dioxide Coupled with Water Oxidation using Various Metal Oxide based Catalytic Systems

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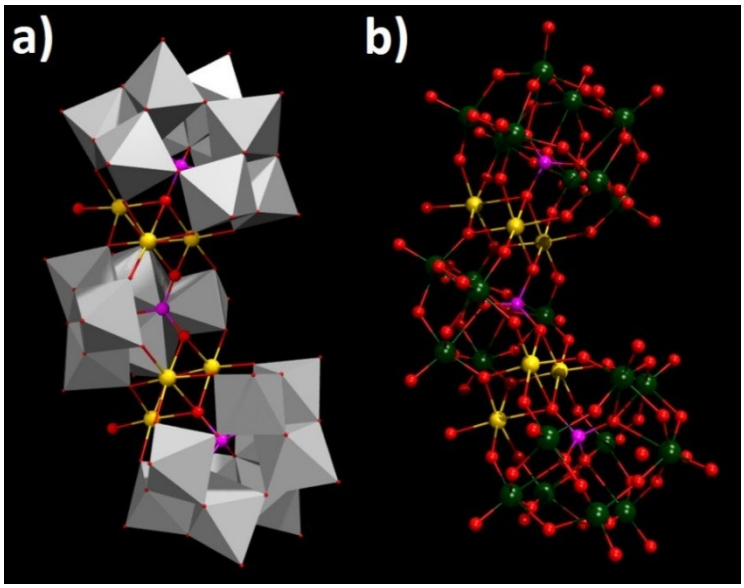

Fig S1. Single Crystal structure of $Mn_6P_3W_{24}$ a) Polyhedral model with Mn-center shown in ball stick representation. b) Ball-stick model. Mn, yellow; P, cyan; W, dark green; O, red.

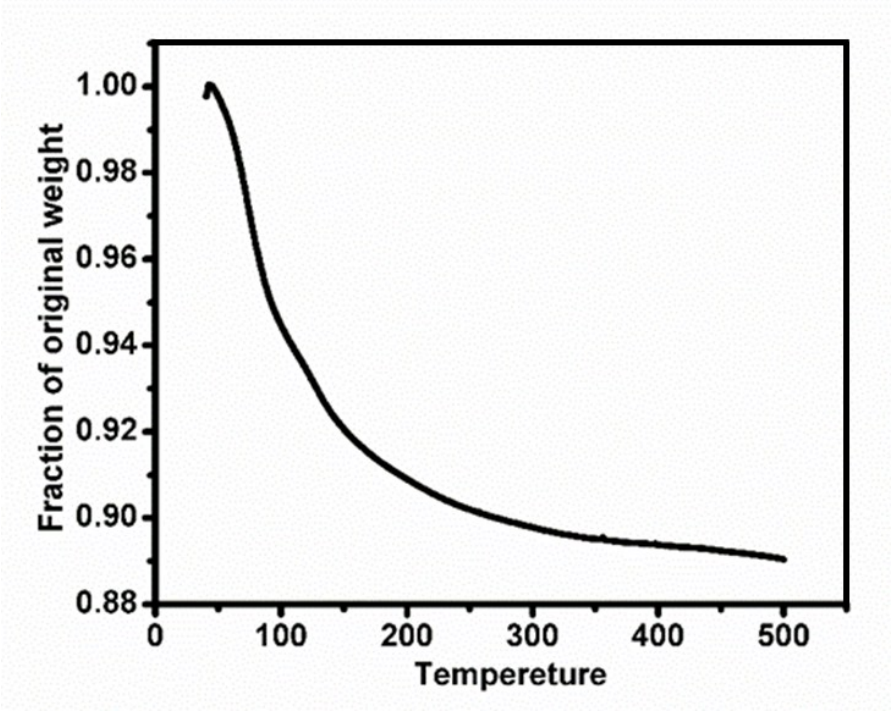

Fig S2. Thermogravimetric analysis (TGA) diagram of $Mn_6P_3W_{24}$

Mn-center	BVS
Mn-1	2.20
Mn-2	2.27
Mn-3	2.23
Mn-4	2.16
Mn-5	2.204
Mn-6	2.32
Total V	13.384

$V = \sum v_i$ where $v_i = \exp((r_o - r)/B)$; r_o = calculated bond distance; r= observed bond distance; B= constant. Its value=.37 . V= valance.

Fig S3. BVS calculation of 6-manganese centres of $[Mn_6P_3W_{24}O_{94}(H_2O)_2]^{17-}$**.**

EPR spectrum of $Mn_6P_3W_{24}$

$Mn_6P_3W_{24}$ shows a broad single line Electron Paramagnetic Resonance (EPR) spectrum (Figure S8) rising around 1850 Gauss and the peak maximum is observed at 3256 Gauss. Single uncoupled manganese is expected to show sextet in EPR spectrum, though sometimes a broad peak is observed at room temperature instead of sextet. In case of $Mn_6P_3W_{24}$ there are 6-Mn(II) centres present with 30 odd electrons, therefore a 31 line EPR spectrum is expected as all Mn-Mn distances in the cluster are longer than 3.4 Å. Here we observe a single broad peak which is quite possibly due to coupling of all 31 peaks. The g value observed for Mn(II) center in $Mn_6P_3W_{24}$ is around 1.97 which is comparatively lower than normal g value observed for Mn(II)-center which is around 2 [4]. Such low g value indicates that manganese centers are not in perfectly octahedral geometry. It implies distortion around octahedral environment of manganese which is also observed in the crystal structure of $Mn_6P_3W_{24}$.

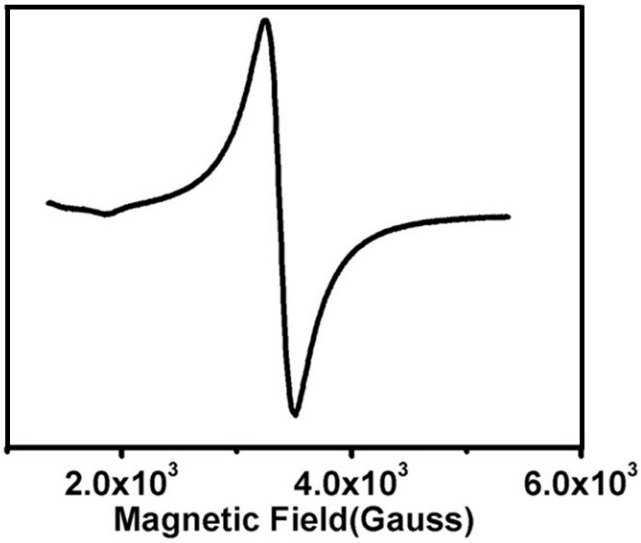

Fig S4. EPR spectrum of $Mn_6P_3W_{24}$ at room temperature.

Single crystal XRD- Table for $Mn_6P_3W_{24}$:

Table S1 |

	Na.**1**
Empirical formula	$Mn_6\ O_{96}\ P_3\ W_{24}$
fw	6769.92
space group (No.)	$P2_1/C$
a (Å)	17.5337(5)
b (Å)	22.2287(7)
c (Å)	35.026(2)
α (deg)	90
β (deg)	95.774(3)
γ (deg)	90
vol (Å^3)	13582.1(10)
Z	4
temp (°C)	-150
wavelength (Å)	0.71073
d_{calcd} (Mg m^{-3})	3.311
abs coeff (mm^{-1})	20.911
R[a] [I > 2ó(I)]	0.0867
Rw[b] (all data)	0.2124

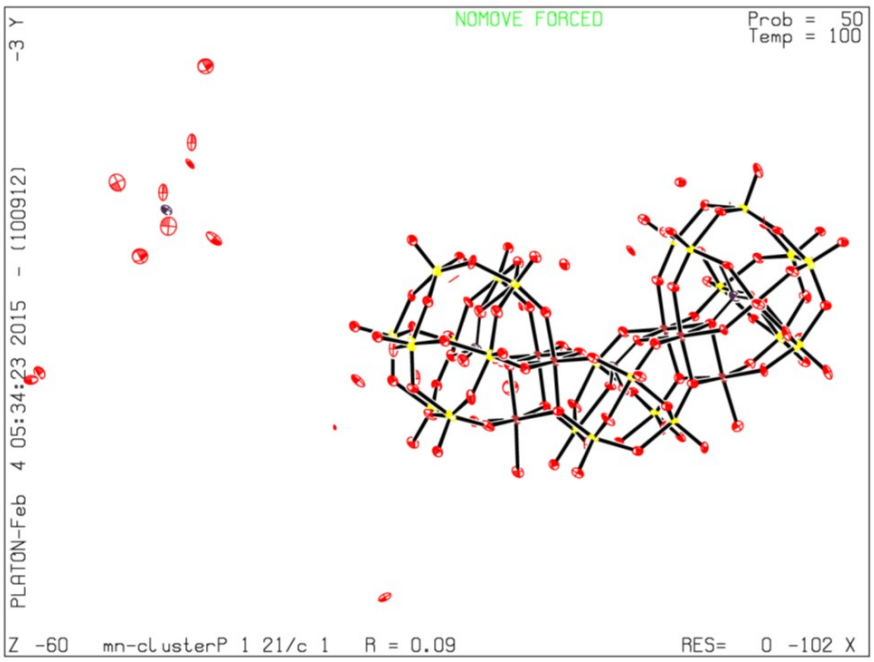

Fig S5. Ellipsoid model of $Mn_6P_3W_{24}$

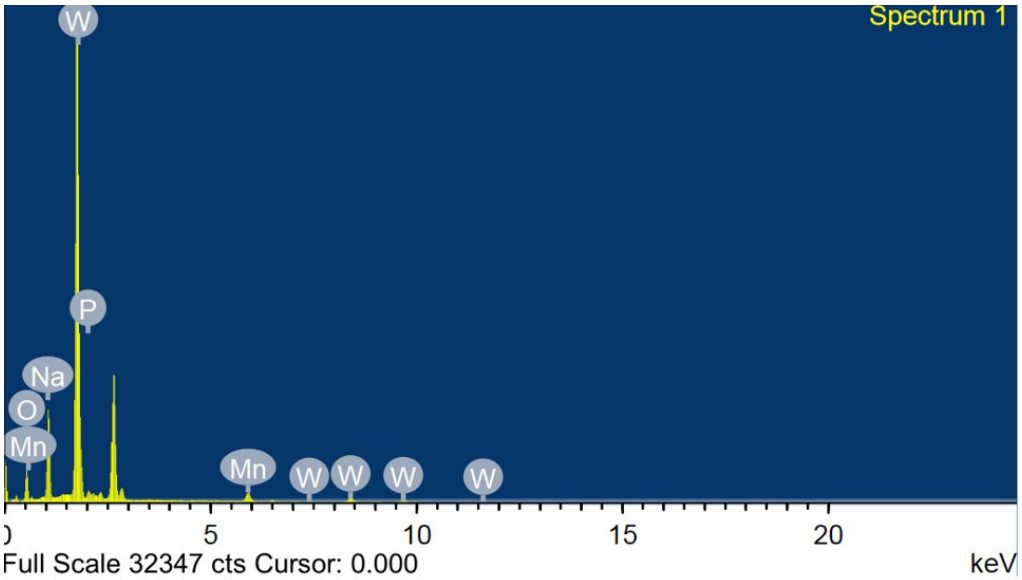

Fig S6. Energy-dispersive X-ray spectroscopy (EDX) of $Mn_6P_3W_{24}$.

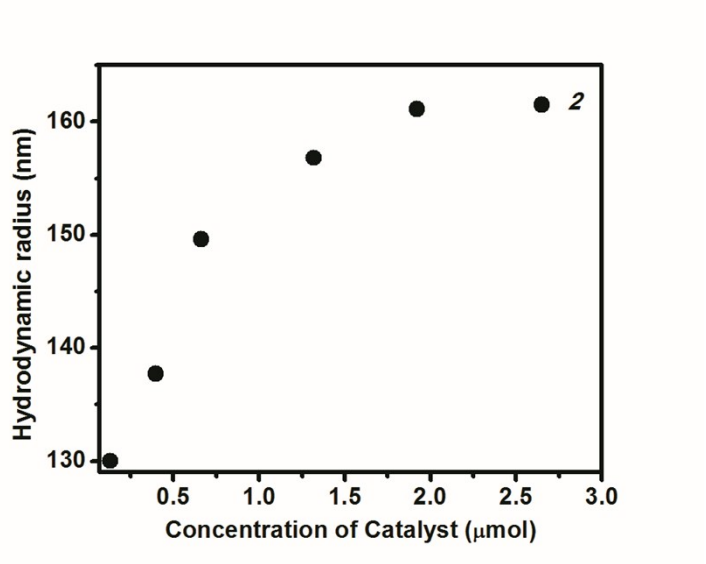

Fig S7. Variation of hydrodynamic radius with catalyst loading taking ***2*** as representative

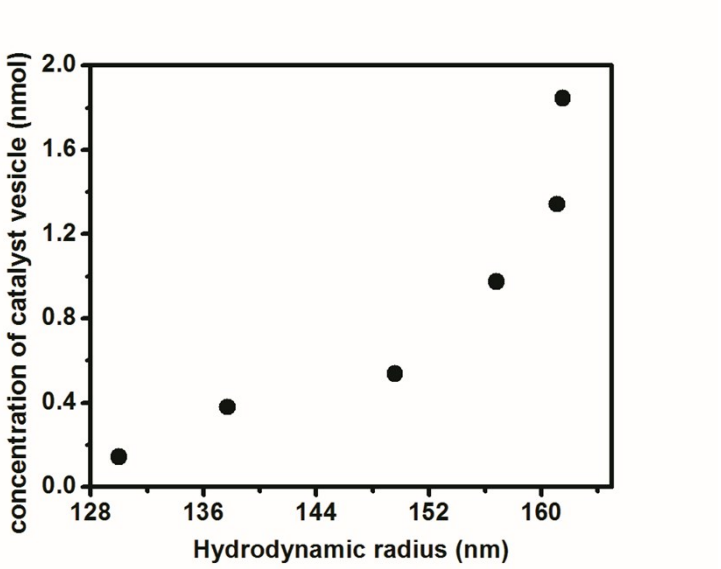

Fig S8. Variation of concentration of catalyst vesicle with hydrodynamic radius of ***2***

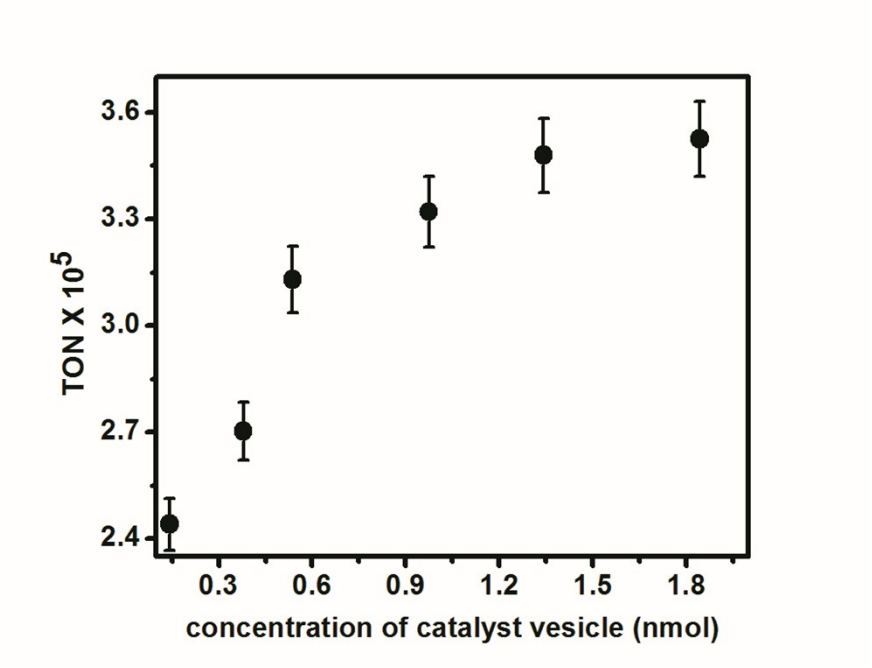

Fig S9. Variation of TON of photochemical CO_2 reduction with change of concentration of catalyst vesicle of ***2***

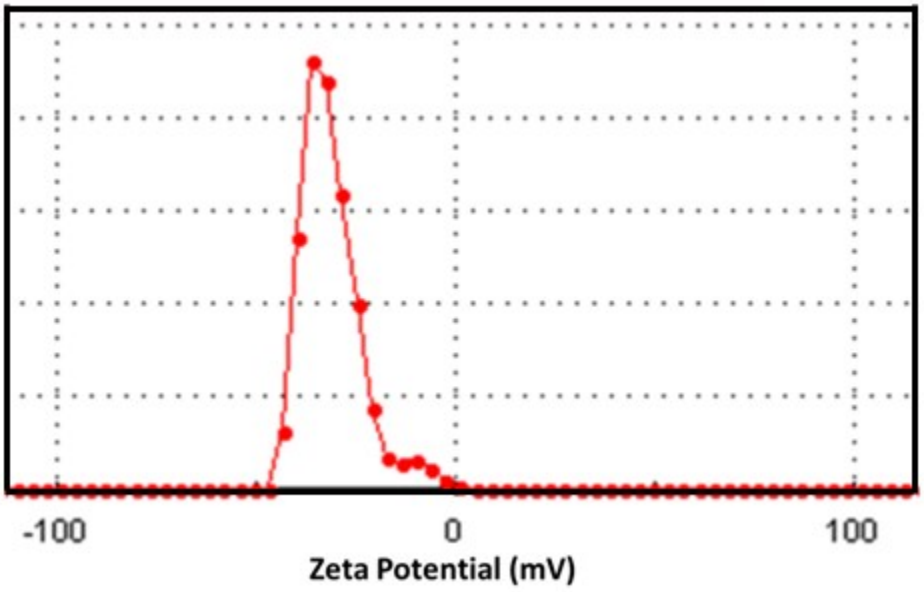

Fig S10. Zeta potential plot of ***3*** in dilute dispersion

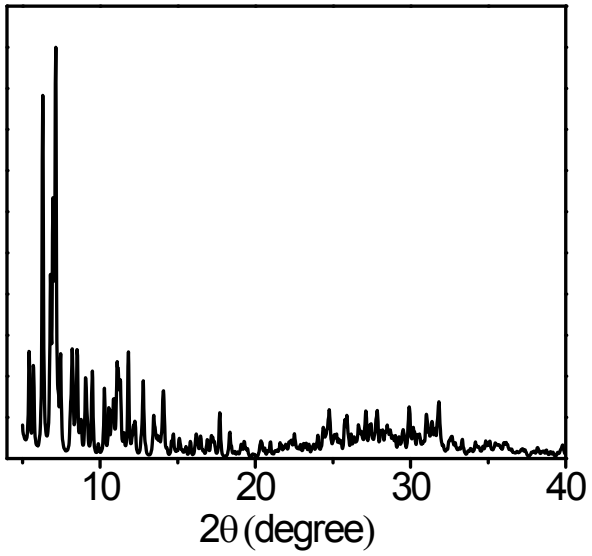

Fig S11. PXRD pattern of Mo_{154}

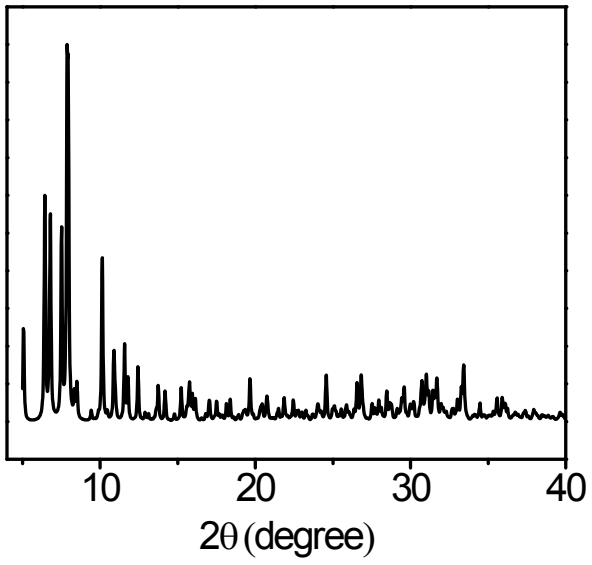

Fig S11. PXRD pattern of $Mn_6P_3W_{24}$

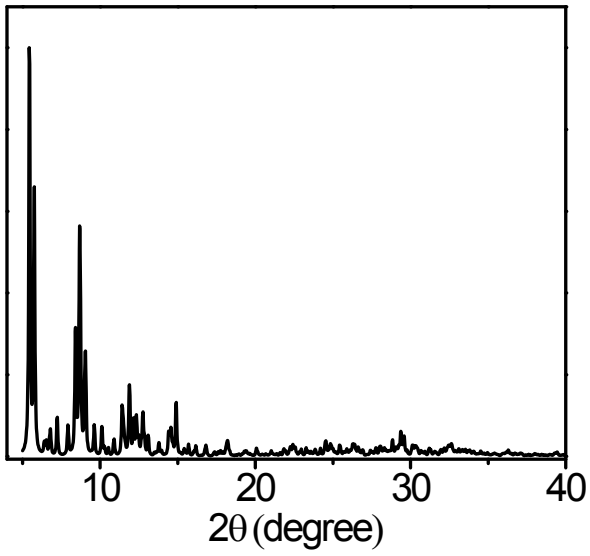

Fig S12. PXRD pattern of Mo_{132}

Stability of catalyst

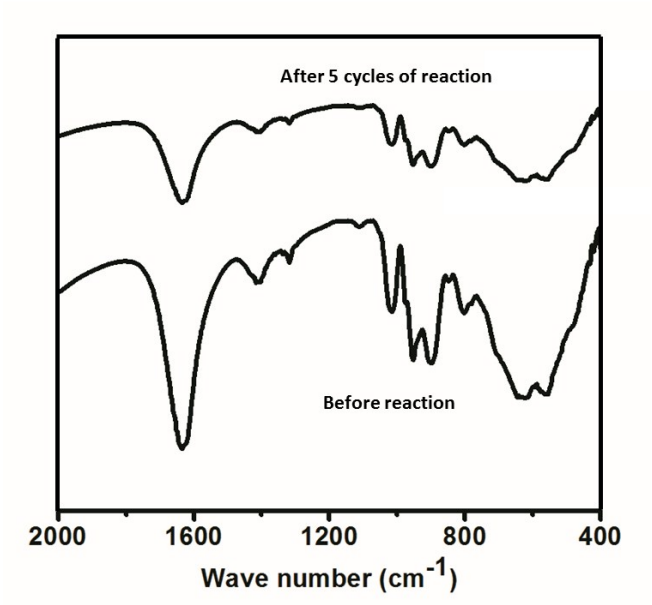

Fig S13. FT-IR spectra of ***1*** after and before reaction, both spectra are identical which indicates that the catalyst is stable in reaction condition.

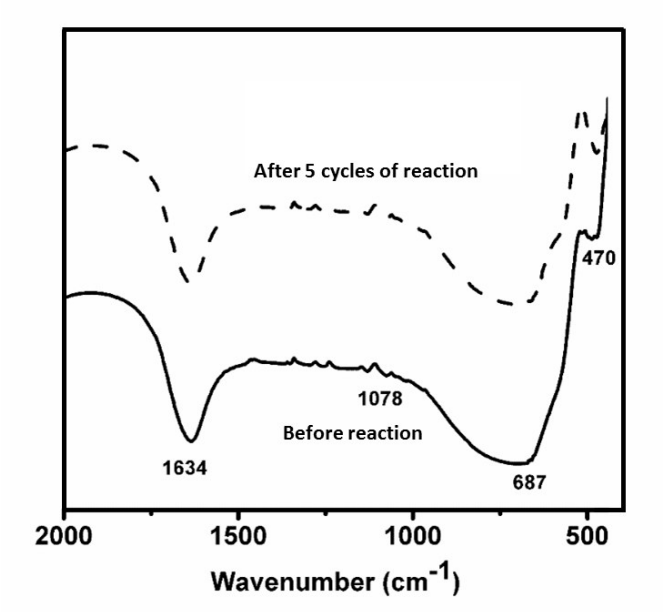

Fig S14. HATR-IR spectrum of ***2,*** solid line represents IR spectrum of ***2*** before reaction and dotted line represents IR spectrum of ***2*** after completion of reaction. Both spectra are identical which indicate that ***2*** is stable under reaction condition.

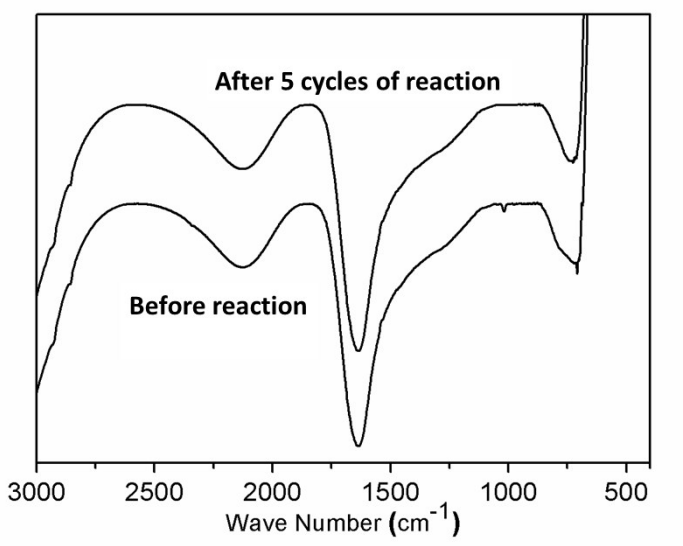

Fig S15. HATR-IR spectrum of ***3*** after and before reaction, both spectra is identical which indicates that the catalyst is stable in reaction condition.

Table S2. Amount of reduced products in various reaction conditions

Catalyst	Amount of catalyst used	Buffer	Amount of formic acid (mmol)	Amount of formaldehyde (mmol)
1	0.15 µmol	pH=5, 0.1 M Acetate	0.116	0.06
Na_2MoO_4	1.5 mmol	pH=5, 0.1 M Acetate	0	0
2	0.15 µmol	pH=5, 0.1 M Acetate	0.0406	0
$Mn(OAc)_2$	1 mmol	pH=5, 0.1 M Acetate	0	0
Na_2WO_4	1 mmol	pH=5, 0.1 M Acetate	0	0
3	0.15 µmol	pH=5, 0.1 M Acetate	0.205	0.18
$(NH_4)_6Mo_7O_{24}$	1 mmol	pH=5, 0.1 M Acetate	0	0
RGO	1 mg/ml	pH=5, 0.1 M Acetate	0	0
Without catalyst	-	pH=5, 0.1 M Acetate	0	0
Mo_{132} (without RGO)	0.15 µmol	pH=5, 0.1 M Acetate	0.08	0.07
1 (without purging CO_2)	0.15 µmol	pH=5, 0.1 M Acetate	0	0